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Note on Dr. Rosenhead's Papers, "The Annual Variation of Latitude" and "Tides on a Two-layer Earth"

By

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Abstract

In both the papers cited above, Dr. Rosenhead refers to my work[1] on "the causes of the annual variation of mean sea level along the Japanese coast", and states, in the former, that the annual variation of latitude can be explained completely by the application of my results, and in the latter that the tides on the yielding earth would be in conflict with my evidence.

If those papers are carefully examined, however, it will be found that the statements mentioned ought to be reversed. That is to say, Rosenhead's results for the tides on a two-layer earth are in harmony with my own results, not in conflict at all, while the paper on latitude variation contains two serious errors—mis-uses of my results—which render his calculations useless. The present paper will show and discuss those misunderstandings and errors.

I. On the Paper on Tides

§ 1. Dr. Rosenhead published an investigation[2] upon the "tides on a two-layer earth" in the Geophysical Supplements to M. N. R. A. S., and stated in it that

> "The work of the present paper appears to indicate that the equilibrium theory can account for the phenomena of the long-period tides, whereas the evidence of Nomitsu and Okamoto indicates the *reverse*—at least for the North Pacific,"

and in the summary also that

1. These Memoirs, A, **10**, 125—161 (1927).
2. Geophys. Suppl. M. N. R. A. S., **2**, 171—196 (1929).

"The values of k and $(1+k-h)$ derived from the long-period tides appear to indicate that the equilibrium theory can account for the long-period tides. This is *in direct conflict* with the experimental evidence of Nomitsu and Okamoto which deals with the annual variation of sea level in the North Pacific."

Seeing these words in much question, however, I examined his paper carefully and found that his work and mine had no direct relation with each other and that the two results are in rather good agreement. It is entirely a misunderstanding on his part to consider that the two are in conflict.

§ 2. Let me here pick out the essential parts of Rosenhead's paper. Assuming the earth as a two-layer globe of Jeffreys' type i. e.

	Outer Shell	Inner Core
Radius	6.37×10^8 cm.$=a$	$0.545a$
Density	4.27 gm./cm.^{3}	12.04 gm./cm.^{3}
Rigidity	1.695×10^{12} dynes/cm.^{2}	0

Rosenhead investigated the effect on the ocean tide of the deformation of the yielding earth produced by the external disturbing forces, once statically and once dynamically. Then he calculated the values of Love's numbers,* h and k, and obtained the following results.

	Statical Theory		Dynamical Theory			
			Fortnightly		Semidiurnal	
	Including the effect of ocean	Neglecting the ocean effect	Ocean depth 2162 m.	8852 m.	2162 m.	8852 m.
h	0.550	0.667	0.583	0.569	0.651	1.706
$c=1+k-h$	0.720	0.697	0.705	0.710	0.468	0.093
k	0.270	0.364	0.288	0.279	0.119	0.799

His conclusion from these results is that the equilibrium theory can account for the phenomena of the long-period tides, although it differs greatly from the real (dynamical) for short-period tides like the semidiurnal.

§ 3. That is true so far, but he goes too far in saying that the evi-

* h=Earth tide/Equilibrium tide corresponding to the disturbing force.
k=Secondary tide due to the deformation of the crust/Equilibrium tide.

dence of Nomitsu and Okamoto indicates the reverse. As the investigation of Rosenhead is an application of Herglotz's method[1] to the yielding earth covered with a *homogeneous* ocean and deals with only such forces as may produce some disturbing action upon the earth crust itself, e. g., the pressure on the sea-bottom, it can have no direct connection with the actual amount of seasonal variation of mean sea level, of which there are various causes but the chief cause is the difference in water-density.

The reason why Rosenhead, notwithstanding this, goes so far beyond the limit to say is probably his misunderstanding of our result that along the Japanese coast the statical effect of the atmospheric pressure is only about a third of the actual variation of mean sea level. He has indeed supposed this to mean that the actual fluctuation of sea level is about three times that of the equilibrium tide corresponding to the disturbing forces—very far from the statical theory.

But that is clearly a surprising misconception of our result unless the barometric variation were the only cause of the whole fluctuation of the sea level. I have however shown that the annual variation of sea level along the Japanese coast is much more effected by the change of water density than by the barometric fluctuation, and that the conjoint effects of these causes all considered *statically* account for the actual motion of the sea level. Moreover as to the influence of water-density, I have preparatorily given a theoretical proof[2] that it might be calculated *statically* if Coriolis' force was neglected. The case where Coriolis' force is considered will be discussed in a forthcoming paper[3].

Thus, the two papers on tides by Rosenhead and myself have no direct connection and they are not opposed at all, but rather in accord in the view that the statical theory can account for the long-period tides.

II. The Paper on Latitude-variation

§ 4. In the Geophysical Supplements Dr. Rosenhead has written also another paper[4] dealing with "the annual variation of latitude" in

1. Zeitschr. f. math. u. phys., **52**, 275 (1905).
2. These Memoirs, A, **10**, 111 (1927).
3. These Memoirs, A, **15**, 131 (1932).
4. Geophy. Suppl. M. N. R. A. S., **2**, 140—170 (1929).

which he states that this phenomenon could be completely explained if, in addition to the causes enumerated in Jeffreys' theory,[1] another and new correction due to oceanic motion were made, employing the results in my paper on the annual variation of mean sea-level.

But examining his paper carefully, one will find two fundamental errors—misuses of my results—which render his calculation futile.

§ 5. In order to explain the points, let us first trace the outline of his work briefly.

Let λ and μ denote angular displacements of the momental axis of the earth from its undisturbed position towards and perpendicular to the Greenwich meridian. Accepting Jeffreys' view that the yearly portion of the latitude variation corresponds to the change of moment of inertia caused by the transference of mass over the earth's surface, Rosenhead obtained from Pollack's analysis[2] of 35-year observations the following values of λ and μ as observed:

$$\left.\begin{aligned} \lambda_{\text{obs.}} &= -0''.0104 \sin\odot - 0''.0028 \cos\odot \\ \mu_{\text{obs.}} &= +0''.0368 \sin\odot - 0''.0010 \cos\odot \end{aligned}\right\} \qquad (1)$$

where $\odot$ represents the sun's longitude.

On the other hand, suppose the annual component of the variable portion of mass per unit area on the earth's surface to be

$$m = \frac{1}{2}\sigma\cos\odot + \frac{1}{2}\sigma'\sin\odot \qquad (2)$$

where σ and σ' are functions of θ the colatitude, and ϕ the longitude east of Greenwich. Then, if the earth were rigid, the corresponding values of λ and μ would be

$$\left.\begin{aligned} \lambda_0 &= -18''.2 \times 10^{-3} \int_0^{\pi}\int_0^{2\pi} m.\ \sin^2\theta\cos\theta \cdot \cos\phi\ d\theta\ d\phi \\ \mu_0 &= -18''.2 \times 10^{-3} \int_0^{\pi}\int_0^{2\pi} m.\ \sin^2\theta\cos\theta \cdot \sin\phi\ d\theta\ d\phi \end{aligned}\right\} \qquad (3)$$

For the actual earth, however, by virtue of its yielding character, these values must be somewhat reduced to such as

$$\lambda = c\lambda_0, \qquad \mu = c\mu_0, \qquad (4)$$

where c is a reduction factor less than 1. According to Rosenhead

1. Monthly Notices Roy. Astr. Soc., **76**, 499—525 (1916); See also "The Earth," 238—249 (1924).

2. Gerlands Beiträge f. Geophys., **16**, 108—194 (1927).

it will be 0.696 for a two-layer earth of Jeffreys' type and approach to 0.6 for many-layer earths.

As such annual changes in the distribution of mass over the earth's surface that could contribute to the latitude variation, Jeffreys enumerated the change of atmospheric pressure, precipitation of snow, and periodic change in vegetation. Besides these three, Rosenhead presumed the change of sea level as a fourth cause, and calculated separately all their contributions to λ_0 and μ_0 by formula (3) getting the following results :—

Causes	λ_0		μ_0	
	Coef. of $\sin\odot$	Coef. of $\cos\odot$	Coef. of $\sin\odot$	Coef. of $\cos\odot$
Precipitation of Snow	+0″.0175	−0″.0238	+0″.0093	−0″.0126
Vegetation	−0″.0038	+0″.0017	−0″.0055	+0″.0024
Atmosphere	+0″.0102	−0″.0020	+0″.0509	−0″.0077
Oceanic Motion	−0″.0393	+0″.0189	+0″.0069	+0″.0165
Sum	−0″.0154	−0″.0052	+0″.0616	−0″.0014

Finally adopting $c=0.6$ in eq. (4), Rosenhead obtained the result

$$\left.\begin{aligned}\lambda &= c\lambda_0 = -0''.0092\sin\odot - 0''.0031\cos\odot \\ \mu &= c\mu_0 = +0''.0370\sin\odot - 0''.0008\cos\odot\end{aligned}\right\} \qquad (5)$$

This is so near to eq. (1) that it makes him consider the problem perfectly solved.

§ 6. Now for the contributions from snow and vegetation in the foregoing table, Jeffreys' values have been accepted without any alteration ; but the remaining contributions from the atmosphere and oceanic motion are the result of Rosenhead's recalculations, in which I perceive two serious mistakes.

One mistake lies in his conception of the contribution from atmospheric pressure. To calculate the barometric contribution he employed also Jeffreys' ingenious method[1] of using only the land values of atmospheric variation, in which it is unnecessary to know the sea values. Namely if m_1 and m_2 be the variable parts of mass due to the barometric variation per unit area over any point of the land and

1. Loc. cit.

sea respectively, then by the law of indestructibility of matter it follows that

$$\int\int_{\text{land}} m_1 dS + \int\int_{\text{sea}} m_2 dS = 0.$$

If we here notice the atmospheric air only, the sea value m_2 as well as the land value m_1 will differ according to locality; but if we consider, after Jeffreys, the atmospheric variation together with the sea motion, which will balance each other *hydrostatically*, then m_2 must be constant all over the ocean and it can be determined by the land values of m_1 only, i. e., from the above equation

$$m_2 = -\frac{\int\int_{\text{land}} m_1 dS}{\int\int_{\text{sea}} dS} = -\overline{m}_1 \frac{\text{Area of land}}{\text{Area of sea}} = -0.40\overline{m}_1, \qquad (6)$$

where $\overline{m}_1$ denotes the mean value of m_1 over the land.

As Rosenhead employed relation (6) to calculate the barometric contribution with eq. (3), his result must necessarily include that part of oceanic motion which keeps *in hydrostatic equilibrium* with the atmospheric pressure. Notwithstanding this, he takes it to represent the effect of the *air only*, and does not subtract that part of oceanic motion taken already into account from his own "correction due to oceanic motion."

§ 7. Secondly his new "correction due to oceanic motion" is entirely a mistake. After introducing the outline and summary of my paper on the annual variation of sea level, Rosenhead surprisingly misinterpret the fact that the whole variation of sea level amounts to about three times that due to the statical effect of barometric pressure. He says

> "The essential point of this paper is that, while the actual and theoretical motions (of ocean water) agree in phase, the amplitude of the actual motion is about three times that of the equilibrium tide,"

as if only the barometric pressure were the total cause of the whole fluctuation of sea level.

This misunderstanding causes him to state

> "The actual variation of sea level is three times that due to barometric variation."

Refering to the surface loading contributing to λ_0 and μ_0, he goes to say,

"An increase of atmospheric pressure will have two effects. The *first effect* will be to increase the surface loading on account of the increased weight of the superposed column of *air*. This effect has already been accounted for in § 4, 2.....

"The *second effect* of the increase in atmospheric pressure is to depress the level of the sea and thus diminish the surface loading. Hence if we analyse the pressure variation over the sea as we have analysed the pressure variation over the land, then we have to *multiply the result by* **-3** to obtain the exact correction to allow for the annual variation of sea level."

In this way indeed, the new correction due to oceanic motion in the foregoing table has been introduced.

But my paper differs absolutely from his understanding of it. I have shown that along the Japanese coast the annual variation of the sea level owes only about one third to the barometric variation, and the remaining greater part to the variations in temperature and salinity, accordingly to the change in the density of water. The one third accompanying the barometric variation has been already accounted for in the contribution to λ_0 and μ_0 in the preceding article. The main part of the fluctuation in level due to the change in water-density does not mean mass-transference over the ocean because it has been proved that the phenomenon can be treated hydrostatically, just like the isostacy in the earth crust, i. e, the sea level stands higher with smaller density and lower with greater density, so that no change in the surface loading contributing to λ_0 and μ_0 will occur.

Although that part of the fluctuation in level due to wind and tributary land water will change the surface loading influencing λ_0 and μ_0, yet their effect will be limited to relatively small coastal seas, and may be negligible in the wide ocean.

From the above discussion it will now be clear that Rosenhead's "correction due to oceanic motion" is entirely erroneous and ought to be erased. Hence as the explanation of latitude variation, his paper marks no further advance than Jeffreys', excepting that it has the merit of having given theoretically the reduction factor c in eq. (4) for yielding earths.

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On the Convection Current and the Surface Level of a Two-layer Ocean

By

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Abstract

In order to find what difference in height of sea-level should be produced by a local difference in the density of sea-water, one[1] of the present authors discussed theoretically in the previous paper the position of the horizontal isobaric layer in the convection current of a two-layer ocean, neglecting Coriolis' force.

The present paper deals with the same problem, taking the influence of the earth's rotation into account, and gives first the formulae for the convection current and then the depth of the horizontal isobaric surface in a rotating ocean of two-layers such as in the previous paper.

According to the result, the ratio of level difference in dynamical equilibrium to that in statical, and hence the depth of the horizontal isobaric layer measured as a fraction of the thickness of the heterogeneous upper part, is equal to unity far more nearly than in the previous case.

Introduction

In the previous paper[2] one of the present authors discussed theoretically the depth of the horizontal isobaric layer in the convection current of a two-layer ocean, and indicated that the local difference in height of sea-level and its seasonal variation due to the difference or variation in the density of sea-water might be generally treated hydrostatically. In that case however, for simplicity, he treated the problem without consideration of the effect of Coriolis' force.

But since this problem is of great importance in the practical

1. Nomitsu, T., On the so-called "Grenzflaeche" in the Current due to the Difference of Density. These Memoirs, **10**, III (1929).

2. Loc. cit.

study of the sea-level, and also has a bearing even on Rosenhead's investigation[1] into the latitude variation, we shall again take up the same problem theoretically, taking the effect of Coriolis' force into account.

Now, for simplicity, let us consider an ocean such that it extends to infinity and consists of two-layers just as in the previous paper, i. e, an upper stratum of a small thickness where the density of water linearly differs from place to place in one horizontal direction, and the lower remaining stratum in which the water is homogeneous throughout.

To find the difference in height of the surface level of such an ocean after the dynamical equilibrium has been reached, it will be enough to determine the depth of the isobaric surface which lies horizontal in the sea. And in order to know the depth of it theoretically, the mathematical formulae for currents in the ocean must be established.

W. Ekman[2] and his collaborator E. Stefansen investigated the problem of the convection current of a two-layer ocean, and gave in the Ann. d. Hydrog. current-diagrams for some special cases without any mathematical illustration, but saying

> " Die ziemlich komplizierten Rechnungen, die hier nicht beschreiben werden können, sind zum grossen Teil von Dr. Elizabeth Stefansen ausgefuhrt."

The diagram is reproduced in Krümmel's Handbuch d. Ozeanographie[3], but there also no information is given about it although the book generally contains so full bibliographies about other problems. Thus we do not know Ekman's own formulae corresponding to the diagram, and we rather think that they have perhaps not yet been published.

As preliminary to our final object, we have ourselves prepared the mathematical equations for the convection current and drawn the current-diagrams. Our diagrams thus obtained are very similar to those of Ekman, but show some differences. Our mathematical calculations also have no such complication as to be called " ziemlich kompliziert." Hence we conjecture there are some differences between

1. Geophys. Suppl. M. N. R. A. S., **2**, 140—170 (1929)
2. Ann. d. Hydrog, 574—575 (1906).
3. Krümmel, Handb. d. Ozeanographie. II, 468 (1911).

Ekman's theory and ours, with respect to either the constitution of the assumed ocean or the boundary conditions taken. For instance, even to the present case of a two-layer ocean, Ekman may have applied his formulae for an entirely heterogeneous sea obtained in the paper of 1905 on the assumption[1] that the horizontal layer of no-pressure-gradient coincides with the no-current layer; but according to our view[2] this is not the case generally, i. e., the horizontal isobaric layer does not always coincide with the no-current layer.

For the above reasons, in the present paper we shall first give our mathematical solutions of the convection currents in a two-layer ocean and then discuss the depth of the horizontal isobaric layer together with the difference of sea-level due to the difference in water-density.

I. Convection Currents in a Two-layer Ocean

§ 1. *Equations for the Currents.*

Let H denote the total depth of the ocean, and let H_1 and $H_2 = H - H_1$ be the thickness of the upper heterogeneous and of the lower homogeneous stratum respectively. In the mean free-surface take the y-axis parallel to the direction of the gradient of density and the x-axis perpendicular to it, and take the z-axis vertically downward.

We shall use the following notation:

ρ = the density of sea-water (use ρ_1 for the upper stratum only, if desired),

μ = the viscosity coefficient,

p = the pressure at a point,

u, v = the component velocities of current in the direction of x and y respectively, and to distinguish the current in the upper heterogeneous and in the lower homogeneous stratum, we use the suffixes 1 and 2 respectively,

t = the time,

ω = the angular velocity of the earth's rotation,

λ = the latitude of the place under consideration,

g = the acceleration due to gravity,

$b = g\dfrac{\partial \rho_1}{\partial y}$ (assume constant throughout the upper stratum),

1. Ekman, V. W., On the influence of the earth's rotation on ocean current. Ark. f. Math. Astr. o. Fys., Bd. 2, Nr. 11. 1905.

2. Nomitsu, On the so called "Grenzfläche" etc. Loc. cit.

d = the depth of the horizontal isobaric layer.

Then the horizontal pressure-gradients in the ocean are

$$-\frac{\partial p}{\partial x}=0,$$

and $$-\frac{\partial p}{\partial y}=b(d-z) \quad \text{for the upper stratum } 0<z<H_1$$
$$=b(d-H_1) \quad \text{for the lower stratum } H_1<z<H.$$

Hence the equations of motion may be written as follows :—

$$\left.\begin{aligned} &\text{For } 0<z<H_1 \\ &\frac{\partial^2 u_1}{\partial z^2}=-2k^2v_1, \quad \frac{\partial^2 v_1}{\partial z^2}=2k^2u_1-a(d-z), \\ &\text{for } H_1<z<H \\ &\frac{\partial^2 u_2}{\partial z^2}=-2k^2v_2, \quad \frac{\partial^2 v_2}{\partial z^2}=2k^2u_2-a(d-H_1), \end{aligned}\right\} \quad \cdots\cdots(1)$$

where $$a=\frac{b}{\mu}=\frac{g}{\mu}\frac{\partial \rho_1}{\partial y} \quad \text{and} \quad k=\sqrt{\frac{\rho\omega\sin\lambda}{\mu}} \quad \cdots\cdots(2)$$

If we introduce a complex variable $w=u+iv$, then equation (1) becomes

$$\left.\begin{aligned} &\frac{\partial^2 w_1}{\partial z^2}=2ik^2w_1-ia(d-z) && 0<z<H_1 \\ &\frac{\partial^2 w_2}{\partial z^2}=2ik^2w_2-ia(d-H_1) && H_1<z<H \end{aligned}\right\} \quad \cdots\cdots(1')$$

The general solutions of (1′) are obviously

$$\left.\begin{aligned} w_1&=\frac{a}{4k^3}[K_1e^{(1+i)kz}+K_1'e^{-(1+i)kz}+2k(d-z)] \\ w_2&=\frac{a}{4k^3}[K_2e^{(1+i)kz}+K_2'e^{-(1+i)kz}+2k(d-H_1)] \end{aligned}\right\} \quad \cdots\cdots(3)$$

where K_1, K_1', K_2 and K_2' are complex arbitrary constants.

Or let

$$\left.\begin{aligned} K_1&=A_1-iB_1, & K_1'&=C_1+iD_1 \\ K_2&=A_2-iB_2, & K_2'&=C_2+iD_2 \end{aligned}\right\} \quad \cdots\cdots(4)$$

then we get

$$\left.\begin{aligned} u_1 &= \frac{a}{4k^3}[A_1e^{kz}\cos kz + B_1e^{kz}\sin kz + C_1e^{-kz}\cos kz + D_1e^{-kz}\sin kz + 2k(d-z)] \\ v_1 &= \frac{a}{4k^3}[A_1e^{kz}\sin kz - B_1e^{kz}\cos kz - C_1e^{-kz}\sin kz + D_1e^{-kz}\cos kz] \\ u_2 &= \frac{a}{4k^3}[A_2e^{kz}\cos kz + B_2e^{kz}\sin kz + C_2e^{-kz}\cos kz + D_2e^{-kz}\sin kz + 2k(d-H_1)] \\ v_2 &= \frac{a}{4k^3}[A_2e^{kz}\sin kz - B_2e^{kz}\cos kz - C_2e^{-kz}\sin kz + D_2e^{-kz}\cos kz] \end{aligned}\right\} \quad \cdots\cdots(3')$$

where A, B, C, D are real constants.

We shall next determine these integration constants with the boundary conditions.

At the free surface ($z=0$), $\left|\frac{\partial w_1}{\partial z}\right|_{z=0}=0$, or from (3)

$$0=(1+i)k(K_1-K_1')-2k$$

$$\therefore \quad K_1-K_1'=\frac{2}{1+i}=(1-i) \quad \cdots\cdots(5)$$

or
$$\left.\begin{aligned} C_1 &= A_1-1 \\ D_1 &= -B_1+1 \end{aligned}\right\} \quad \cdots\cdots(5')$$

At the intermediate surface of discontinuity ($z=H_1$),

$$0=|w_1-w_2|_{z=H_1} \quad \text{or} \quad 0=(K_1-K_2)e^{(1+i)kH_1}+(K_1'-K_2')e^{-(1+i)kH_1}$$

and

$$0=\left|\frac{\partial w_1}{\partial z}-\frac{\partial w_2}{\partial z}\right|_{z=H_1}$$

or $$0=(K_1-K_2)e^{(1+i)kH_1}-(K_1'-K_2')e^{-(1+i)kH_1}-\frac{2}{1+i}$$

$$\therefore \quad (K_1-K_2)e^{(1+i)kH_1}=-(K_1'-K_2')e^{-(1+i)kH_1}=\frac{1-i}{2} \quad \cdots\cdots(6)$$

Separating these values into real and imaginary parts, we have

$$(A_1-A_2)\cos kH_1+(B_1-B_2)\sin kH_1=\frac{1}{2}e^{-kH_1}$$

$$(A_1-A_2)\sin kH_1-(B_1-B_2)\cos kH_1=-\frac{1}{2}e^{-kH_1}$$

$$(C_1-C_2)\cos kH_1+(D_1-D_2)\sin kH_1=-\frac{1}{2}e^{kH_1}$$

$$(C_1-C_2)\sin kH_1-(D_1-D_2)\cos kH_1=-\frac{1}{2}e^{kH_1}$$

$$\therefore\quad \left.\begin{aligned} A_2 &= A_1-\frac{1}{2}e^{-kH_1}(\cos kH_1-\sin kH_1)\\ B_2 &= B_1-\frac{1}{2}e^{-kH_1}(\cos kH_1+\sin kH_1)\\ C_2 &= C_1+\frac{1}{2}e^{kH_1}(\cos kH_1+\sin kH_1)\\ D_2 &= D_1-\frac{1}{2}e^{kH_1}(\cos kH_1-\sin kH_1)\end{aligned}\right\}\quad\cdots\cdots(6')$$

Thus, if we know only two, A_1 and B_1, of these eight integration constants, then the other six can be at once calculated by equations (5′) and (6′).

Next, the bottom condition of the real ocean may be some intermediate one between that there is no bottom-current and that no bottom-friction exists, so it will be sufficient to treat these two extreme cases.

In this article we shall first treat the *case where no bottom-current exists*, that is

$$0=|w_2|_{z=H}\quad\text{or}\quad K_2e^{(1+i)kH}+K_2'e^{-(1+i)kH}+2k(d-H_1)=0\qquad(7)$$

Substitute (5) and (6) in (7), then

$$0=\left[K_1-\frac{(1-i)}{2}e^{-(1+i)kH_1}\right]e^{(1+i)kH}$$
$$+\left[K_1-(1-i)+\frac{(1-i)}{2}e^{(1+i)kH_1}\right]e^{-(1+i)kH}+2k(d-H_1)$$

$$\therefore\quad K_1=A_1-iB_1$$
$$=\frac{1}{2\cosh(1+i)kH}\left[(1-i)\left\{\sinh(1+i)k(H-H_1)+e^{-(1+i)kH}\right\}\right.$$
$$\left.+2k(H_1-d)\right]\quad\cdots\cdots(8)$$

But
$$\frac{1}{2\cosh(1+i)kH}=\frac{\cosh(1-i)kH}{2\cosh(1+i)kH\cosh(1-i)kH}$$
$$=\frac{\cosh kH\cos kH-i\sinh kH\sin kH}{\cosh 2kH+\cos 2kH}$$

$$(1-i)\cosh(1-i)kH=(\cosh kH\cos kH-\sinh kH\sin kH)$$
$$-i(\cosh kH\cos kH+\sinh kH\sin kH)$$

and $$\sinh(1+i)k(H-H_1)+e^{-(1+i)kH}=\sinh k(H-H_1)\cos k(H-H_1)$$
$$+e^{-kH}\cos kH+i\left\{\cosh k(H-H_1)\sin k(H-H_1)-e^{-kH}\sin kH\right\}$$

$$\therefore\quad A_1=\frac{1}{\cosh 2kH+\cos 2kH}\Big[2k(H_1-d')\cosh kH\cos kH$$
$$+(\cosh kH\cos kH-\sinh kH\sin kH)\times$$
$$\{\sinh k(H-H_1)\cos k(H-H_1)+e^{-kH}\cos kH\}$$
$$+(\cosh kH\cos kH+\sinh kH\sin kH)\times$$
$$\{\cosh k(H-H_1)\sin k(H-H_1)-e^{-kH}\sin kH\}\Big]\ldots\ldots\ldots(9)$$

$$B_1=\frac{1}{\cosh 2kH+\cos 2kH}\Big[2k(H_1-d')\sinh kH\sin kH$$
$$-(\cosh kH\cos kH-\sinh kH\sin kH)\times$$
$$\{\cosh k(H-H_1)\sin k(H-H_1)-e^{-kH}\sin kH\}$$
$$+(\cosh kH\cos kH+\sinh kH\sin kH)\times$$
$$\{\sinh k(H-H_1)\cos k(H-H_1)+e^{-kH}\cos kH\}\Big]\ldots\ldots\ldots(10)$$

Thus, all integration constants are expressed in the terms of H, H_1, and k which define the constitution of the ocean.

Of the current represented by eq. (3′) together with (9) and (10), the part which corresponds to $d=0$ may be called "pure convection current", and the remaining part, which contains the terms of d' only, is nothing but a "slope current" given by Ekman.

§ 2. *Deep Sea in which* $e^{-k(H-H_1)}\ll 1$

In the real ocean, H is very large while H_1 is very small compared with H, so that $e^{-k(H-H_1)}$ and e^{-kH} may be neglected as compared with 1.

In such cases the formulae for the calculation of coefficients in the preceding Art. can be much simplified. That is to say, from (9), (10) and (5′) we obtain

$$\left.\begin{aligned} A_1 &= \frac{1}{2}e^{-kH_1}(\cos kH_1 - \sin kH_1) \\ B_1 &= \frac{1}{2}e^{-kH_1}(\cos kH_1 + \sin kH_1) \\ C_1 &= A_1 - 1 \\ D_1 &= -B_1 + 1 \end{aligned}\right\} \quad \cdots\cdots(11)$$

and from (6′)

$$\left.\begin{aligned} A_2 &= 0 \\ B_2 &= 0 \\ C_2 &= C_1 + \frac{1}{2}e^{kH_1}(\cos kH_1 + \sin kH_1) \\ D_2 &= D_1 - \frac{1}{2}e^{kH_1}(\cos kH_1 - \sin kH_1) \end{aligned}\right\} \quad \cdots\cdots(12)$$

Moreover since, as will be shown in the following Art.,[1] in such a deep sea the depth of the horizontal isobaric layer d is nearly equal to H_1, the current equations (3′) will be reduced to

$$\left.\begin{aligned} u_1 &= \frac{a}{4k^3}\Big\{2A_1\cosh kz\cos kz + 2B_1\sinh kz\sin kz + e^{-kz}(\sin kz - \cos kz) \\ &\qquad + 2k(H_1 - z)\Big\} \\ v_1 &= \frac{a}{4k^3}\Big\{2A_1\sinh kz\sin kz - 2B_1\cosh kz\cos kz + e^{-kz}(\cos kz + \sin kz)\Big\} \\ u_2 &= \frac{a}{4k^3}\Big\{C_2\cos kz + D_2\sin kz\Big\}e^{-kz} \\ v_2 &= \frac{a}{4k^3}\Big\{-C_2\sin kz + D_2\cos kz\Big\}e^{-kz} \end{aligned}\right\} \quad (13)$$

The above formulae (11), (12), (13) are all functions of H_1, but do not contain H. Thus it is to be noticed that the convection current in such a deep sea will be determined by the thickness of the heterogeneous stratum and the gradient of the density of sea-water only, but it is independent of the total depth H.

For example, let us consider the cases where the thickness of the heterogeneous stratum H_1 is equal to $\frac{1}{4}D$, $\frac{1}{2}D$, D and $1.25D$ respectively, D being the "depth of wind current" or "depth of the frictional influence" as it is called by Ekman.

1. See § 4, the case where $S_y = 0$.

Then $kH_1 = \frac{\pi}{4}, \frac{\pi}{2}, \pi, 1\frac{1}{4}\pi$, since $D = \frac{\pi}{k}$.

The corresponding values of coefficients in the current formulae are given by eqs. (11) and (12) as follows:—

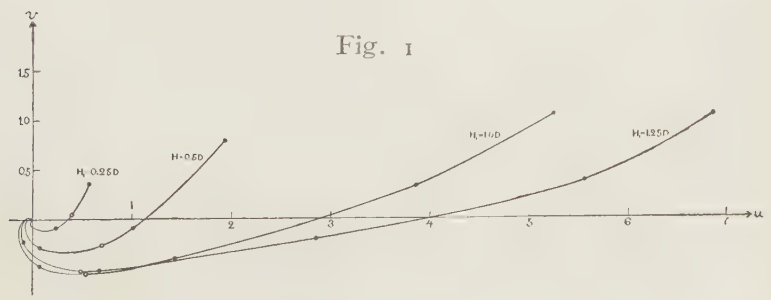
kH_1	$\pi/4$	$\pi/2$	π	1.25π
A_1	0	−0.1039	−0.0216	0
B_1	+0.3224	+0.1039	−0.0216	−0.0139
C_1	−1	−1.1039	−1.0216	−1
D_1	+0.6776	+0.8961	+1.0216	+1.0139
C_2	+0.5509	+1.3013	−12.592	−36.894
D_2	+0.6776	+3.3014	+12.592	+1.0139

Substituting these in eq. (13), and calculating the values of u and v at $z = H_1$ and at the intervals of $0.4D$ from surface to depth $4D$, we get the following table, in which, for simplicity, $\frac{a}{4k^3}$ is taken as unit velocity.

kH_1 / kz	$\frac{\pi}{4}$		$\frac{\pi}{2}$		π		$1\frac{1}{4}\pi$	
	u	v	u	v	u	v	u	v
0	+0.571	+0.355	+1.934	+0.792	+5.240	+1.043	+6.854	+1.028
0.4π	+0.232	−0.090	+1.008	−0.082	+3.861	+0.318	+5.591	+0.375
0.8π	−0.004	−0.071	+0.072	−0.278	+1.431	−0.391	+2.841	−0.158
1.2π	−0.020	−0.005	−0.069	−0.044	+0.064	−0.407	+0.674	−0.520
1.6π	−0.003	+0.005	−0.018	+0.015	−0.105	−0.054	−0.080	−0.230
2.0π	+0.001	+0.001	+0.003	+0.006	−0.024	+0.024	−0.070	+0.002
2.4π	+0.000	−0.000	+0.002	+0.000	+0.003	+0.008	−0.007	+0.015
2.8π	—	—	+0.000	−0.000	+0.003	+0.000	+0.001	+0.001
3.2π	—	—	—	—	+0.000	−0.000	+0.000	−0.000
3.6π	—	—	—	—	—	—	—	—
4.0π	—	—	—	—	—	—	—	—
kH_1	+0.396	+0.041	+0.686	−0.270	+0.544	−0.544	+0.499	−0.527

Drawing hodographs with these values, we obtain Fig. 1.

Fig. 1



In the diagram, the thick lines correspond to currents in the upper heterogeneous stratum and the thin lines to currents in the lower homogeneous part. Comparing this diagram with that of Ekman and Stefansen, we perceive some difference in them notwithstanding much resemblance in the main features. We can not judge, however, whether the difference originates from the fundamental assumptions in the theory or merely from the process of approximation in the numerical calculation, because we do not know Ekman's current formulae.

From the above table or graph, we get also the shallowest depth at which velocity v becomes nil, as follows :—

H_1	0.25 D	0.5 D	1.0 D	1.25 D
z where $v=0$	1.20 H_1	0.74 H_1	0.58 H_1	0.60 H_1

Thus we notice that the layer of no-current in y-direction will be tolerably different from the horizontal isobaric surface explained in the next Chapter.

II. Depth of the Horizontal Isobaric-layer

§ 3. *Total Flow S*

In order to determine the depth of the isobaric layer which lies horizontal, we must prepare the integration of current from surface to bottom i. e., the total flow of current.

Let S_x and S_y be the total flow in the direction of x and y respectively, that is

$$S_x = \int_0^{H_1} u_1 dz + \int_{H_1}^{H} u_2 dz,$$

$$S_y = \int_0^{H_1} v_1 dz + \int_{H_1}^{H} v_2 dz.$$

And let S denote the resultant of the above two components, then

$$S = S_x + iS_y = \int_0^{H_1} w_1 dz + \int_{H_1}^{H} w_2 dz$$

$$= \frac{a}{4k^3}\left[\frac{1}{(1+i)k}(K_1 e^{(1+i)kz} - K_1' e^{-(1+i)kz}) - k(d-z)^2\right]_0^{H_1}$$

$$+\frac{a}{4k^3}\left[\frac{1}{(1+i)k}(K_2'e^{(1+i)kz}-K_2'e^{-(1+i)kz})\right.$$
$$\left.+2k(d-H_1)z\right]_{H_1}^{H}$$
$$=\frac{a}{4k^4}\left[\frac{1-i}{2}\left\{K_2'e^{(1+i)kH}-K_2'e^{-(1+i)kH}\right.\right.$$
$$+(K_1-K_2)e^{(1+i)kH_1}$$
$$\left.-(K_1'-K_2')e^{-(1+i)kH_1}-(K_1-K_1')\right\}$$
$$\left.+k^2\left\{2(d-H_1)(H-H_1)-(d-H_1)^2+d^2\right\}\right] \quad \text{.....(14)}$$

Substituting (5) and (6) in this, we finally get[1]

$$S=\frac{a}{4k^4}\left[(1-i)K_1\sinh(1+i)kH+i\left\{\cosh(1+i)k(H-H_1)-e^{-(1+i)kH}\right\}\right.$$
$$\left.+k^2\left\{H_1^2-2H(H_1-d)\right\}\right] \quad \text{.....(15)}$$

Or putting A_1-iB_1 instead of K_1, and separating the equation into two parts, real and imaginary, we have

$$S_x=\frac{a}{4k^4}\left[A_1(\cosh kH\sin kH+\sinh kH\cos kH)\right.$$
$$+B_1(\cosh kH\sin kH-\sinh kH\cos kH)$$
$$-\left\{\sinh k(H-H_1)\sin k(H-H_1)+e^{-kH}\sin kH\right\}$$
$$\left.+k^2\left\{H_1^2-2H(H_1-d)\right\}\right] \quad \text{.....(16)}$$

$$S_y=\frac{a}{4k^4}\left[A_1(\cosh kH\sin kH-\sinh kH\cos kH)\right.$$
$$-B_1(\cosh kH\sin kH+\sinh kH\cos kH)$$
$$\left.+\left\{\cosh k(H-H_1)\cos k(H-H_1)-e^{-kH}\cos kH\right\}\right] \quad \text{.....(17)}$$

If the sea is so deep that $e^{-k(H-H_1)}$ is negligible compared with 1, the above equations reduce to

1. Though S, S_x, S_y can be expressed in simpler form by using equation (7), we adopt the form of (15) because it is rather convenient for calculation of the horizontal isobaric layer.

$$S_x=\frac{a}{4k^2}\left\{H_1^2-2H(H_1-d)\right\} \quad \cdots\cdots(16')$$

$$S_y=0 \quad \cdots\cdots(17')$$

§ 4. *Determination of d corresponding to* $S_y=0$

Suppose a case where the earth is covered throughout with an ocean of uniform depth, and the density of sea-water varies from equator to pole according to latitude only. Or conceive another case in which a long straight coast exists and from every part of it land-water spreads equally far off. In both cases the total flow in the direction of gradient of density must be zero when the sea has reached a steady state.

Thus in many important cases we may take the equation of continuity as

$$S_y=\int_0^{H_1} v_1 dz+\int_{H_1}^{H} v_2 dz=0 \quad \cdots\cdots(18)$$

The calculation of this equation may be executed by substituting eqs. (9) and (10) for A_1 and B_1 in eq. (17), but it is easier to use the complex eqs. (15) and (8). That is, the terms which contain A_1 and B_1 in eq. (17) correspond to the imaginary parts in the following expression

$$(1-i)K_1\sinh(1+i)kH=\frac{\sinh(1+i)kH\cosh(1-i)kH}{2\cosh(1+i)kH\cosh(1-i)kH}\times$$

$$\left[\begin{matrix}(1-i)^2\{\sinh(1+i)k(H-H_1)+e^{-(1+i)kH}\}\\+(1-i)2k(H_1-d)\end{matrix}\right]$$

$$=\frac{\sinh 2kH+i\sin 2kH}{\cosh 2kH+\cos 2kH}\times$$

$$\left[\begin{matrix}-i\{\sinh k(H-H_1)\cos k(H-H_1)+e^{-kH}\cos kH\}\\+\cosh k(H-H_1)\sin k(H-H_1)-e^{-kH}\sin kH+(1-i)k(H_1-d)\end{matrix}\right].$$

Hence eq. (18) becomes

$$0=-\sinh 2kH\left\{\sinh k(H-H_1)\cos k(H-H_1)+e^{-kH}\cos kH\right\}$$

$$+\sin 2kH\left\{\cosh k(H-H_1)\sin k(H-H_1)-e^{-kH}\sin kH\right\}$$

$$-k(H_1-d)(\sinh 2kH-\sin 2kH)$$

$$+(\cosh 2kH+\cos 2kH)\Big\{\cosh k(H-H_1)\cos k(H-H_1) - e^{-kH}\cos kH\Big\}.$$

From this, the formula for the depth of the horizontal isobaric layer is given by

$$\frac{H_1-d}{H_1}=$$

$$\frac{\cosh k(H+H_1)\cos k(H-H_1)+\cosh k(H-H_1)\cos k(H+H_1)-2\cosh kH\cos kH}{kH_1(\sinh 2kH-\sin 2kH)} \quad \cdots\cdots(19)$$

Especially when the ocean is very deep but its heterogeneous stratum is very thin as compared with the whole depth, the above equation may be written as

$$\frac{H_1-d}{H_1}\fallingdotseq 2\,\frac{(\cosh kH_1\cos kH_1-1)\cos kH+\sinh kH_1\sin kH_1\sin kH}{kH_1e^{kH}}, \quad (19')$$

and hence d is very nearly equal to H_1, and even $(H_1-d)H$ tends to zero as H increases indefinitely.

On the other hand, if the heterogeneous stratum extends to the bottom i. e., $H=H_1$, we have

$$\frac{H_1-d}{H_1}=\frac{\cosh 2kH+\cos 2kH-2\cosh kH\cos kH}{kH(\sinh 2kH-\sin 2kH)}, \quad \cdots\cdots(19'')$$

and in this case d/H_1 is nearly equal to $\frac{3}{8}=0.375$ for a very shallow sea, and approaches to 1 for a very deep ocean.

The general tendency of the values of d/H_1 will be shown in the following table and Fig. 2.

From the table we see that as the total depth H increases in comparison with D or H_1, the value of d/H_1 approaches to unity more rapidly than in the previous paper which neglected the effect of Coriolis' force.

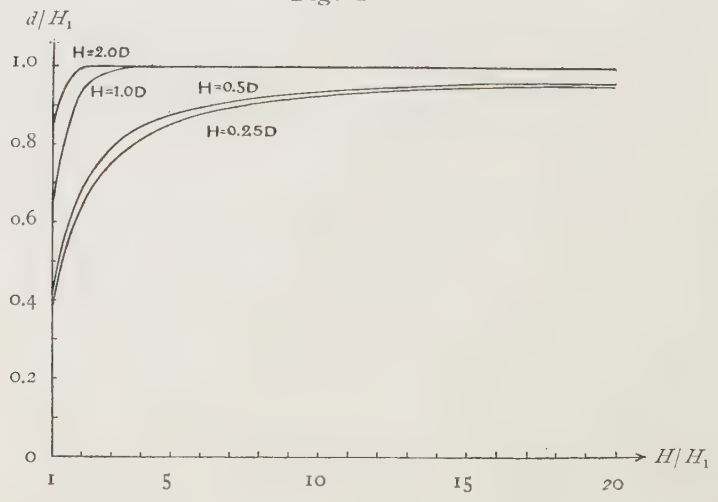
Now since d/H_1 corresponds to the ratio of level difference due to the density inequality in dynamical equilibrium to that in statical, we can conclude as follows.

The rule that difference or variation in the height of sea-level due to the local inequality or variation of the density of sea-water

Values of d/H_1

H/H_1 \ H/D	$\frac{1}{4}$	$\frac{1}{2}$	1	2	4	6	8	10	20	$\to\infty$
1	0.378	0.417	0.653	0.841	0.920	0.947	0.960	0.968	0.984	1.000 $=1-\frac{1}{kH}$
2	0.639	0.688	0.945	1.014	1.000	1.000	1.000	1.000	1.000	
4	0.812	0.844	0.993	1.002						
6	0.877	0.896	0.998	1.000						
8	0.906	0.922	0.999							
10	0.927	0.937	1.000							
12	0.939	0.948								
14	0.946	0.955				All the blanks = 1.000				
16	0.953	0.961								
18	0.958	0.965								
20	0.962	0.969								
∞	1.000	1.000								

Fig. 2



may be calculated statically, is much more strongly confirmed by taking Coriolis' force into account than by neglecting it.

There remains a matter that calls for a little more explanation. On rare occasions, according to the values of H and H_1, e. g., when $H=2D$ and $H/H_1=2$ or 4 in the above table, the formula (18) gives a value of d/H_1 which exceeds unity by a very small amount. Mathematically this is possible and forms no objection to the foregoing

treatment, as far as the said boundary conditions and differential equation (2) hold.

From the physical point of view, however, since d/H_1 must not become greater than unity, such an ocean would not strictly reach the steady state indicated by differential equation (2) and the boundary conditions.

Nevertheless, if we notice that the excess over unity is very slight and that such a case always lies between possible cases in which d/H_1 is smaller than unity, we may say that even though such a sea might not exactly reach a steady state, it will fluctuate so near the state corresponding to the above solution that the deviation may be neglected.

Lastly for a very deep sea, since $(H_1-d)H$ tends to zero, eq. (16′) may be written as

$$S=S_x=\frac{a}{4k^2}H_1^2=\frac{g\dfrac{\partial\rho_1}{\partial y}}{4\rho\omega\sin\lambda}H_1^2 \quad \text{.....(16″)}$$

§ 5. *Case of an Enclosed Sea.*

If an enclosed sea is in a steady state, the total flow must be zero in the direction of x as well as y. In this case a surface-slope γ_x will generally be produced in the direction of x also, in addition to the slope, $\gamma_y=\frac{1}{\rho}\frac{\partial\rho_1}{\partial y}\cdot d$, in the y-direction corresponding to d. Consequently there should result a slope-current, of which total flow is given by Ekman[1] as follows :—

$$S_x'=\frac{g\cdot\sin\gamma_x}{4k\omega\sin\lambda}\cdot\frac{\sinh 2kH-\sin 2kH}{\cosh 2kH+\cos 2kH} \quad \text{.....(20)}$$

$$S'_y=\frac{g\cdot\sin\gamma_x}{4k\omega\sin\lambda}\cdot\left(\frac{\sinh 2kH+\sin 2kH}{\cosh 2kH+\cos 2kH}-2kH\right) \quad \text{.....(21)}$$

Then the equations of continuity for an enclosed sea will be

$$S_x+S'_x=0 \quad \text{.....(22)}$$

$$S_y+S'_y=0 \quad \text{.....(23)}$$

where S_x and S_y are to be taken from eqs. (16) and (17).

By these two equations (22) and (23), we can easily determine the two quantities γ_x and d.

1. Loc. cit.

If we put for simplicity

$$\left.\begin{aligned} F&=\sinh 2kH-\sin 2kH \\ G&=\sinh 2kH+\sin 2kH-2kH(\cosh 2kH+\cos 2kH) \\ P&=\sinh k(H+H_1)\sin k(H-H_1)+\sinh k(H-H_1)\sin k(H+H_1) \\ &\quad -2\sinh kH\sin kH+k^2H_1^2(\cosh 2kH+\cos 2kH) \\ Q&=\cosh k(H+H_1)\cos k(H-H_1)+\cosh k(H-H_1)\cos k(H+H_1) \\ &\quad -2\cosh kH\cos kH \\ m&=\frac{b}{g\rho k}=\frac{1}{\rho}\frac{\partial\rho_1}{k\partial y}, \end{aligned}\right\} \quad \cdots\cdots(24)$$

then eqs. (22) and (23) take form

$$\left.\begin{aligned} F.\sin\gamma_x+m[P+G.k(H_1-d)]&=0 \\ G.\sin\gamma_x+m[Q-F.k(H_1-d)]&=0 \end{aligned}\right\},$$

from which we get

$$\left.\begin{aligned} k(H_1-d)&=\frac{FQ-GP}{F^2+G^2} \\ \sin\gamma_x&=-m\frac{FP+GQ}{F^2+G^2} \end{aligned}\right\} \quad \cdots\cdots(25)$$

Especially when the sea is very deep ($e^{-kH}\ll 1$), the above equations give

$$\left.\begin{aligned} &\gamma_x=0 \\ &H_1-d=\frac{H_1^2}{2H}, \quad \text{or} \quad \frac{d}{H_1}=1-\frac{H_1}{2H} \end{aligned}\right\} \quad \cdots\cdots(25')$$

III. Case of no Bottom-friction

§ 6. *The Currents*

Hitherto we have assumed the bottom-current zero as the bottom-condition. Next let us consider what difference will occur if we adopt the condition that there is no friction at the sea-bottom.

All the equations up to (6) are also applicable to this case, but eq. (7) must be replaced by

$$0=\left|\frac{\partial w_2}{\partial z}\right|_{z=H}=K_2e^{(1+i)kH}-K_2'e^{-(1+i)kH} \quad \cdots\cdots(26)$$

Substitute (5) and (6) in (26), then we have

$$K_1 = A_1 - iB_1$$

$$= \frac{(1-i)\{\cosh(1+i)k(H-H_1) - e^{-(1+i)kH}\}}{2\sinh(1+i)kH} \quad \cdots\cdots(27)$$

or

$$A_1 = \frac{1}{(\cosh 2kH - \cos 2kH)} \Big[(\sinh kH\cos kH - \cosh kH\sin kH) \times \Big\{ \cosh k(H-H_1)\cos k(H-H_1) - e^{-kH}\cos kH \Big\}$$

$$+ (\sinh kH\cos kH + \cosh kH\sin kH) \times \Big\{ \sinh k(H-H_1)\sin k(H-H_1) + e^{-kH}\sin kH \Big\} \Big] \quad \cdots\cdots(28)$$

$$B_1 = \frac{1}{(\cosh 2kH - \cos 2kH)} \Big[(\sinh kH\cos kH + \cosh kH\sin kH) \times \Big\{ \cosh k(H-H_1)\cos k(H-H_1) - e^{-kH}\cos kH \Big\}$$

$$- (\sinh kH\cos kH - \cosh kH\sin kH) \times \Big\{ \sinh k(H-H_1)\sin k(H-H_1) + e^{-kH}\sin kH \Big\} \Big] \quad \cdots\cdots(29)$$

Combining these equations with (5′), (6′) and (3′), we can determine the currents u and v.

§ 7. *The Total Flow and the Horizontal Isobaric-layer*

Let us now calculate the total flow $S = S_x + iS_y$. In the present case, all the terms containing Ks in eq. (14) will cancel one another, and there remains

$$S = S_x + iS_y = \frac{a}{4k^2}\Big\{H_1^2 - 2H(H_1 - d)\Big\}$$

$$\therefore \quad \left.\begin{aligned} S_x &= \frac{a}{4k^2}\Big[H_1^2 - 2H(H_1 - d)\Big] \\ S_y &= 0 \end{aligned}\right\} \quad \cdots\cdots(30)$$

Hence, the condition $S_y = 0$ can not determine the depth of the horizontal isobaric layer.

If, however, there is any circumstance such as to make $S_x = 0$, e. g. as in an enclosed sea, the corresponding value of d will be given by

$$\frac{d}{H_1} = 1 - \frac{H_1}{2H} \quad \cdots\cdots(31)$$

This coincides with the result[1] obtained in the previous paper for the same bottom-condition but without taking Coriolis' force into account.

It must be here noticed that eqs. (31) and (25′) are identical in form but quite different in nature. There is no limitation of H and H_1 for eq. (31), while eq. (25′) is restricted to a very deep sea with a comparatively thin heterogeneous upper stratum. For example eq. (31) can be used even when $H_1 = H$, and it gives

$$\frac{d}{H_1} = \frac{1}{2} = \frac{4}{8}$$

Summary

We have investigated the currents and the horizontal isobaric surface in a two-layer ocean, taking the effect of the earth's rotation into account, and the chief results obtained are as follows.

1. Though the currents are similar to the diagram given by Ekman and Stefansen, there seems to be some difference. Since Ekman's mathemetical formulae are not known, we can not find where the origin of the difference will lie.

2. Generally speaking, the layer in which the velocity (v) in the direction of the gradient of density is nil, does not coincide with the layer in which the horizontal pressure-gradient is nil.

3. In a tolerably deep sea the ratio of the depth of the horizontal isobaric layer (d) to the thickness of the heterogeneous stratum (H_1) will be practically equal to unity, except when H_1 is nearly equal to the total depth H.

This rule is made more decisive and conspicuous by the action of Coriolis' force.

4. When local inequality of density extends from surface to bottom i. e. $H = H_1$, the ratio d/H_1 becomes minimum and may attain a value from $\frac{3}{8}$ to $\frac{4}{8}$ according to the bottom condition and the depth of the sea. This least value of d/H_1 coincides with that in the case where Coriolis' force is neglected.

5. It follows from the third item that in a deep ocean the level

1. Nomitsu, loc. cit. p. 118, eq. (16).

difference or its variation due to the difference in density of sea-water can be treated statically. The rule proves more decisive and more reliable in the present paper than in the previous paper.

6. The only exception is such a sea that the depth is very small and the difference in density or its variation extends nearly to the sea bottom. The level-difference or variation calculated statically will be too large to represent the actual state. The actual value will sometimes be only $\frac{3}{8}$ to $\frac{4}{8}$ of the statical one. The effect of the earth's rotation in this case hardly exists.

7. If the sea is sufficiently deep, and if there is no circumstance for producing a surface-slope in the x-direction and the equation of continuity demands only $S_y=0$, then the total flow in the direction perpendicular to the gradient of water-density will take the value

$$S_x = \frac{g\frac{\partial \rho_1}{\partial y}}{4\rho\omega\sin\lambda} H_1^2,$$

where λ is the latitude and ρ_1 the density of water in heterogeneous part.

Electrolytic Reduction of Saccharin. Part I. Electrolysis in Acid and Alkaline Solutions

By

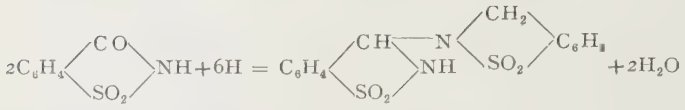
Motooki Matsui, Tetsunosuke Sawamura and Teruzo Adachi

(Received February 17, 1932)

Not long ago B. Sakurai[1] reported that phthalimide easily undergoes reduction electrolytically, and that one of the two carbonyl groups changes first into the corresponding secondary alcoholic group and then into the methylene group, as is generally seen in the reduction of the carbonyl compounds. Judging from its analogous composition, saccharin may be expected to behave chemically in a similar manner, yet an attempt made by Remsen and Burton[2] to reduce it with tin and hydrochloric acid was reported to have ended in failure. The present authors thought it might be very interesting, therefore, to determine experimentally how saccharin differs from phthalimide in its behavior towards electrolytic reduction.

The electrolytic reduction of saccharin in an acid solution was observed to differ entirely from that in an alkaline solution, which splitt off the sulphonyl group from the benzene ring in the form of sulphurous acid and produced benzamide and its reduction products, such as benzaldehyde and hydrobenzoin. Reduction in an acid solution may be regarded to have taken place in such a way that the carbonyl group was transformed into the methylene group through the stage of the secondary alcohol group. Still, the intermediate hydroxybenzylsultam[3] itself could never be isolated, being always produced condensed with the ultimate reduction product, thus—

1. Bull. Chem. Soc., Japan, **5**, 184 (1930).
2. I. Remsen and M. Burton: Am. Chem. Jour. **11**, 403 (1889).
3. The nomenclature proposed by P. Fritsch [Ber. **29**, 2290 (1896)] is used here because of its brevity.



It is here to be noted that the same condensation product was also obtained by J. Koetschet[1] who, with the object of preparing saccharin, oxidized o-toluol sulphamide using p-toluol dichlorsulphamide as the oxidizing agent.

Experimental

I. Electrolysis was first conducted by taking a solution, which consisted of 50 c.c. of 15% sulphuric acid, 50 c.c. of alcohol and 5 grams of saccharin, as the catholyte and 15% sulphuric acid as the anolyte. A lead plate of 70 sq. cms. was used as the cathode, and a current of 5.5 amperes was passed at 15°—18° for 3 hours. The anode was also of lead. On electrolysing under agitation of the cathode solution, saccharin, at first suspended in the catholyte, gradually disappeared, and the solution, which had been pale yellow in colour, became colourless. The current was then cut, and the catholyte was nearly neutralized with caustic soda and evaporated to drive off alcohol. On the solution being cooled, a reduction product crystallized out. By purifying it by recrystallization from hot water a substance melting at 141° was obtained. It was analysed with the following results:

0.1169 gm. of the substance gave 0.2131 gm. CO_2 and 0.0397 gm. H_2O. 0.1000 gm. of the substance produced ammonia for neutralization of which 8.5 c.c. of $\frac{1}{14}$N-HCl was required.

	C	H	N
Found (%)	49.74	3.80	8.50
Calc. for $C_{14}H_{12}O_4N_2S_2$ (%)	50.00	3.60	8.30

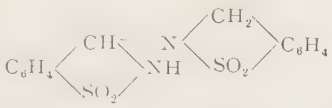
Its molecular weight was found to be 345 (Calc., 336) by the ebullioscopic method, ethyl alcohol being used as the solvent.

0.0078 gm. of the substance in 12.0208 gms. alcohol raised the B. P. of alcohol by 0.002°.

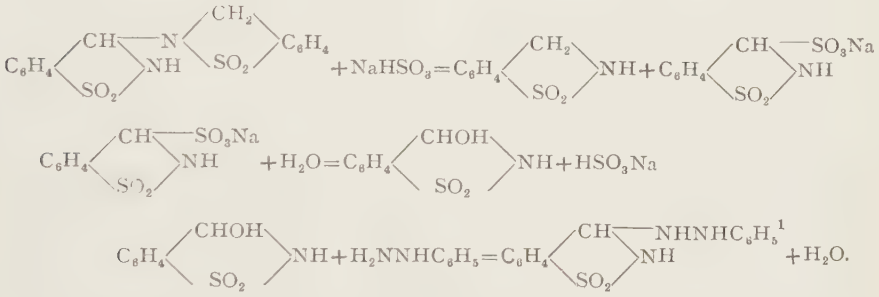
It is soluble in alcohol, acetone, alkali and hot water; sparingly so in benzene, chloroform and ether. On further electrolytic reduction

1. J. and P. Koetschet: Helv. Chimi. Acta, **12**, 669 (1929).

it changes into benzylsultam and on oxidation into saccharin. When its alkaline solution is saturated with sulphurous acid gas and left to stand, benzylsultam crystallizes out. From the solution separated from the crystals of benzylsultam, a phenylhydrazine compound of hydroxybenzylsultam is easily obtainable as fine yellow needles by first neutralizing it with an acid and then treating it with phenylhydrazine. Judging from these properties and also from the results of analysis, the reduction product is evidently a condensation product of the formula.



Its reaction with phenylhydrazine may be conceived to proceed according to the following scheme:



In this electrolysis the concentration of acid and the current density do not much affect the reduction, but the temperature must always be maintained below 30°. The use of zinc, mercury and zinc amalgam as the cathode has no significant effect if the other conditions of electrolysis are not altered.

II. A series of electrolyses was now undertaken with the object of obtaining a still further reduced product by increasing both the current density and the concentration of acid and at the same time raising the temperature to 50°. The concentration of sulphuric acid was doubled and a current of 1 ampere/10 sq. cms. was passed for 2 hours. The catholyte after electrolysis was treated just in the same manner as in 1, and a substance crystallizing in needles and melting at 107° was obtained. It was analysed with the following results:

1. This phenylhydrazine compound was also prepared by Koetschet, who named it the phenylhydrazone of pseudo-o-sulphamidboenzaldehyde.

0.1261 gm. of the substance gave 0.2276 gm. CO_2 and 0.0483 gm. H_2O. 0.1151 gm. of the substance produced ammonia for neutralization of which 9.7 c.c. of $\frac{1}{14}$-N-HCl was required.

	C	H	N
Found (%)	49.24	4.29	8.43
Calc. for $C_7H_7O_2NS$ (%)	49.70	4.10	8.30

It is soluble in alcohol, ether, acetone, chloroform and hot water, far less so in carbon bisulphide and benzene. When oxidized with potassium permanganate it changes into saccharin. All these properties well agree with those possessed by one of the decomposition products obtained from the above mentioned condensation product.

Whether the reduction goes on to benzylsultam or stops at the formation of the intermediate condensation product, chiefly depends on the temperature at which the electrolysis is carried out. This was confirmed by several experiments performed with the object of making this relation clear.

III. In all the experiments above described, hydroxybenzylsultam could, in no case, be obtained in the free state. The use of copper as the electrode was also found fruitless. Perhaps this is due to the fact that hydroxybenzylsultam and saccharin undergo reduction with nearly equal ease, and the former is very liable to enter into a condensation reaction with its reduction product. From such a point of view it was attempted to catch hydroxybenzylsultam in some combined form as quickly as it was formed, by electrolysing saccharin in the presence of phenylhydrazine. The conditions of electrolysis were the same as in 1. except the concentration of sulphuric acid, the percentage of which was lowered from 15% to 10%. About 3.5 grams of phenylhydrazine was added to the catholyte. As the electrolysis went on, a yellow substance began to separate out and accumulated in the cathode compartment. It crystallized from alcohol in fine yellow needles melting at about 197° and was identified as the phenylhydrazone of pseudo-o-sulphamidobenzaldehyde obtained by Koetschet[1]. When further electrolysed at a higher temperature (50°), the concentration of sulphuric acid and the current density being at the same time raised, as in II, it was readily reduced to benzylsultam completely.

1. loc. cit.

IV. Finally, electrolysis in an alkaline solution was carried out, 3% caustic soda solution being taken as the catholyte and a sodium carbonate solution as the anolyte. Both electrodes were of lead and a current of 3 amperes/70 sq. cms. was passed for an hour at 15°–18°. By treating the catholyte after electrolysis with chloroform, a quantity of white shining crystals melting at 127° was obtained with the material yield of 65%. On its properties being examined, the substance was found to be benzamide. It having been thus found that electrolysis in an alkaline solution splitt off the sulphonyl group from the benzene ring, the catholyte from which the benzamide had been extracted was acidified with hydrochloric acid, when a considerable evolution of sulphurous acid gas was recognized.

When the electrolysis was continued longer than an hour the catholyte began to evolve ammonia gas and at the same time to show the presence of benzaldehyde. It is hardly necessary to say that, as some of the benzaldehyde condenses into benzoin, reduction of the latter substance also takes place simultaneously so as to produce hydrobenzoin. Benzaldehyde was confirmed as its phenylhydrazone melting at 156° and hydrobenzoin as stilbene bromide melting at 237°.

The results of electrolytic reduction of saccharin in a neutral solution will be reported in the near future.

On the Tides and Seiches of Osaki-Bay

By

Yoshikazu Toyohara

(Received February 17, 1932)

1. Introduction

Osaki-Wan, immediately south of Wakanoura-Wan, is a small bay penetrating far into the land and measuring about 3 sq. kilometres in area; it is very deep—18 metres in the deepest part and 11.7 metres on an average. As it is, moreover, surrounded by hills, strong winds seldom, if ever, blow here. The range of tide attains more than 2 metres all over its coast.

Our tidal-station stands on the right shore of Osaki-ura in the north-west corner of the Bay (Fig. 1. ○), and it is very favourable for tidal observation, having a depth of 8 metres only a few metres from the beach. The situation calculated from the trigonometrical survey bench mark shown in Charts[1] No. 59 and No. 98 is

$34^\circ\ 7'\ 46''.7$ N. $135^\circ\ 7'\ 41''.1$ E.

We have here a self-recording tide-gauge (reduction 1/10) of the Kelvin type and have been carrying out observations since July 1st 1926.

For the correction of time we always compare it with a Rassel Co.'s chronometer, and determine the rate of the chronometer by the radio time-signal.

The standard level is taken as 180.9 cms. beneath a mark on the third step of the inner wall of the observation well.

As five years have elapsed since the commencement of our observations, I shall report here some results of our observations in that time.

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1. Chart published by the Hydrographic Department of Japan, No. 59. No. 98.

Fig. 1

2. Variations of the Monthly and Yearly Mean Sea-level

From the tidal-records for the five years we read off the hourly heights of sea-level, and calculated the monthly mean level, the result being as follows.

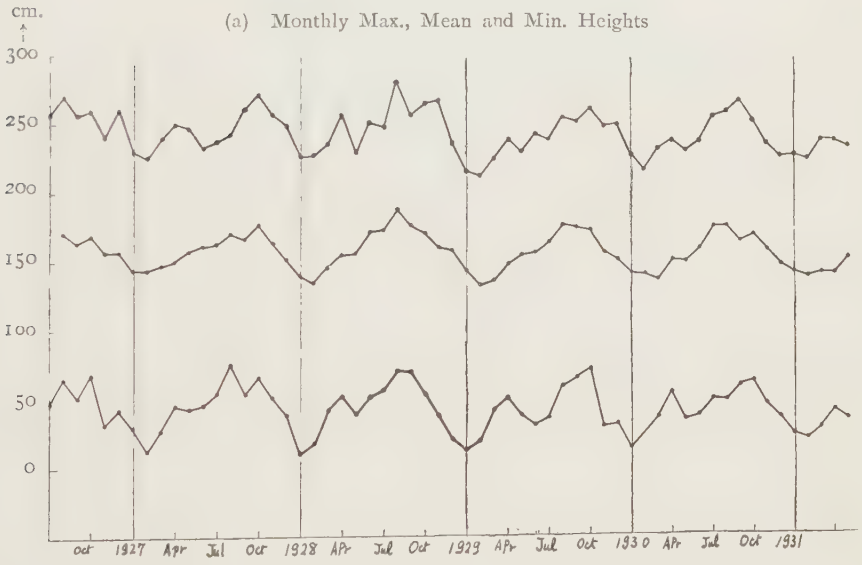
Monthly Means of Sea-level.

Year / Month	1926	1927	1928	1929	1930	1931	Total	Mean
		cm.	cm.	cm.	cm.	cm.	cm.	cm.
Jan.		144.72	140.00	145.02	142.61	143.92	716.27	143.254
Feb.		144.12	135.07	134.00	141.71	140.10	695.00	139.000
Mar.		147.43	145.62	138.29	138.09	142 51	711.94	142.388
Apr.		149.44	154.47	148.44	152.96	142.71	748.02	149.604
May.		157.79	155.57	155.57	151.76	153.46	774.15	154.830
Jun.		161.40	171.35	158.09	160.40	158.99	810.23	162.046
Jul.	cm.	162.71	173.97	165.22	176.68	164.42	843.00	168.600
Aug.	171.65	170.55	188.44	178.59	176.58		885.81	177.162
Sep.	164.02	166.83	176.58	175.37	165.83		848.63	169.726
Oct.	169.95	170.05	170.35	173.46	170.85		854.66	170.932
Nov.	157.58	163.92	160.50	157.68	160.00		799.68	159.936
Dec.	157.58	151.65	158.99	152.56	148.94		769.72	153.944
Total	820.78	1890.61	1930.91	1882.29	1886.41	1046.11	9457.11	1891.422
Mean	(164.156)	157.551	160.909	156.858	157.201	(149.444)	788.093	157.619

The difference between the maximum and the minimum height every month is about 2 metres on an average, and that between the heighest (282.4 cms. on Aug. 18th 1928) and the lowest (10.1 cms. on Jan. 8th 1928) during the five years reaches 272.3 cms.

Fig. 2a, b, c show the variations of the monthly mean, the monthly maximum and the minimum and also the yearly mean of sea level.

Fig. 2



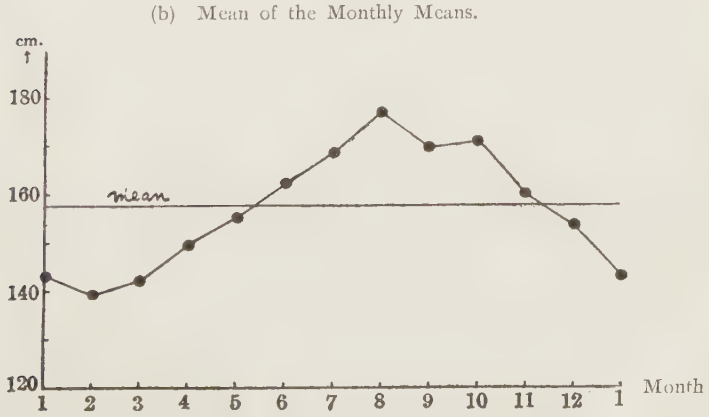
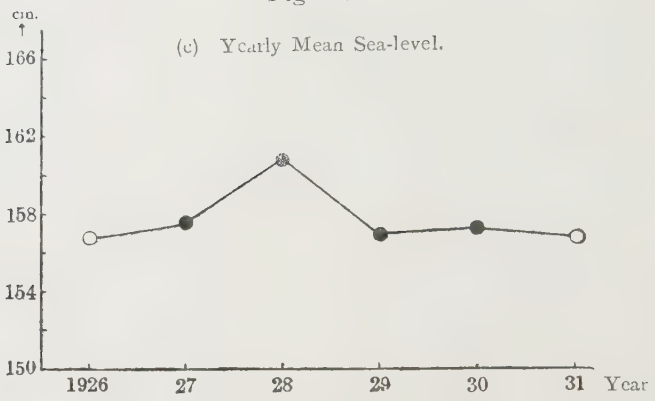


Fig. 2.



3. Tidal Constants at Osaki

The tidal constants determined from the data obtained in about one year from Oct. 1st 1929 by Darwin's Method[1] are as follows:

Harmonic Constants of Tides
Osaki, Japan.
34° 7′ 46″.7 N. 135° 7′ 41″.1 E.
(Epoch 1929 Oct. 1)

Tide	H	x	Tide	H	x
	cm.	o		cm.	o
Sa	17.405	151.33	K_2	5.762	197.90
Ssa	0.278	239.11	M_1	0.564	128.38
S_1	1.408	72.99	M_2	45.621	180.22
S_2	21.770	205.39	M_3	0.721	184.03
S_4	0.174	99.30	M_4	0.341	67.57
S_6	0.088	231.95	M_6	0.524	163.14
P	7.814	189.96	O	18.546	171.24
K_1	23.904	187.93	N	9.231	173.95
T	1.741	248.20	Q	3.811	161.38
R	0.346	152.15			

These values seem to be accord with the tidal constants of various ports about the Kii Channel which were determined some years ago by Dr. S. Hirayama[2] and by Dr. S. Ogura[3] and also with that of Port Shimotsu recently published by Mr. T. Hidaka.[4]

1. G. H. Darwin: Scientific Papers, Vol. I. Oceanic Tides. (1907).
2. S. Hirayama: Memoirs Coll. Science, Tokyo. **28**, No. 7 (1911).
3. S. Ogura: 日本近海ノ潮汐 (1914).
4. T. Hidaka: Jour. Oceanography, Kobe Marine-Meteo. Obs., **1**, 377 (1929).

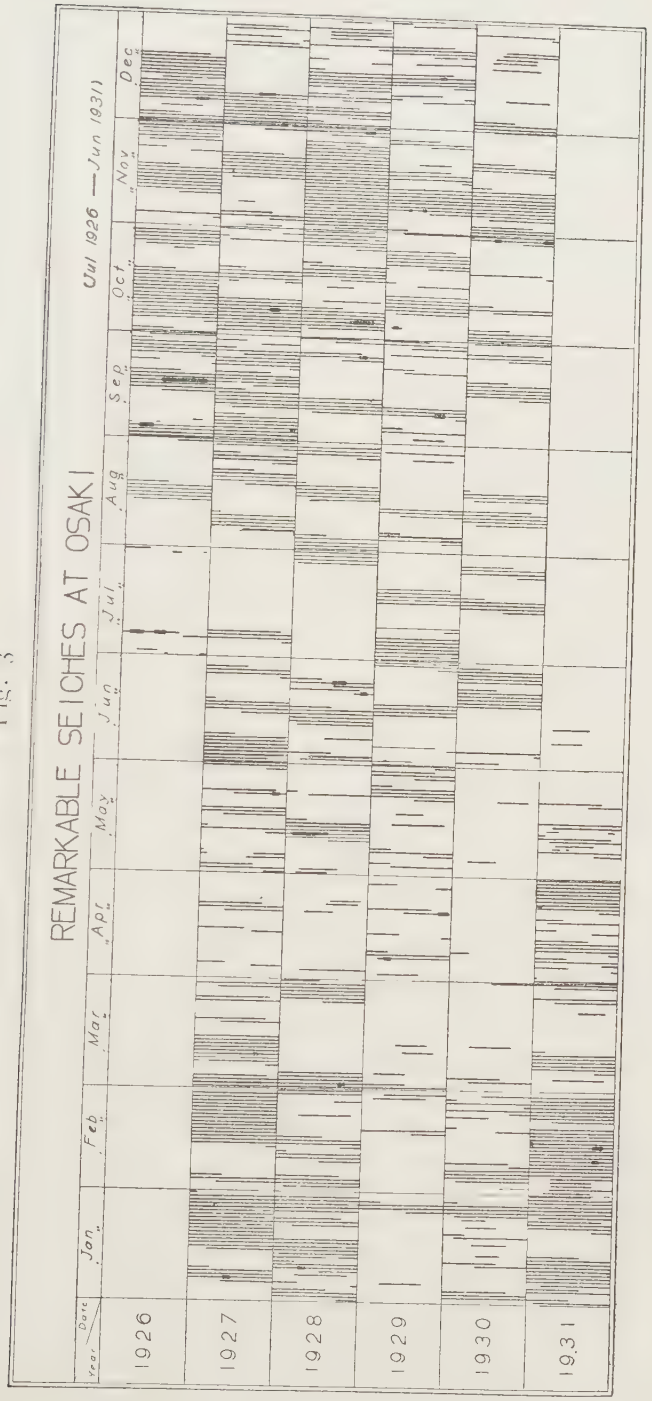

REMARKABLE SEICHES AT OSAKI
Jul 1926 — Jun 1931
Year
Date
Jan.
Feb.
Mar.
Apr.
May
Jun.
Jul.
Aug.
Sep.
Oct.
Nov.
Dec.
1926
1927
1928
1929
1930
1931

Fig. 3

4. Seiches of Osaki-Bay

Owing to the complexity of shape and the great depth of the Bay, seiches of various periods frequently develop well.

On our marigram, remarkable seiches were recorded 247 times in five years and 29 of those indicate amplitudes of over 20 cms. It is usually between late autumn and winter that these seiches appear and some of them often last for more than ten days.

Fig. 3 shows the dates of occurrence and the time of duration of the chief seiches of the past five years, the thick lines in it corresponding to those which had amplitudes of over 20 cms.

In most cases seiches of various periods are superposed on one another, but if we choose only 170 records in which the periods can be easily read off, and classify the number of occurrences according to the period, we get eight groups as Fig. 5 shows.

Fig. 4

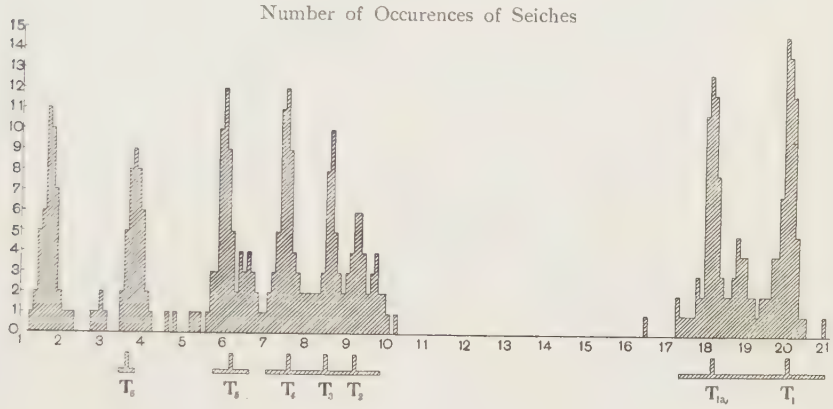
Looking over the shape and the depth of the bay, let us consider the following portions of sea (Fig. 4), as the oscillating areas that may produce the above eight kinds of seiche.

For each area we calculate the mean depth h and measure the length of the major axis L from the chart, and determine the corresponding period of free oscillation, using the well known formula $T=\frac{4L}{\sqrt{gh}}$ (for the transversal oscillation T_{VI} use $T=\frac{2L}{\sqrt{gh}}$) and performing on it a mouth correction after Rayleigh. The results are shown in the following table:—

	Area	Node	Length (L)	Breadth (B)	Mean depth (h)	Period
			km.	km.	min.	
1	ABCDNE″A	$\overline{AB}$	2.6	1.3	12.3	$T_I=19.9\pm0.9$
2	LB′CDNE″L	$\overline{LB}$	2.4	1.0	12.3	$T_{Ia}=18.1\pm0.8$
3	LNEGHIJL	$\overline{LN}$	1.0	0.9	9.2	$T_{II}=9.2\pm0.6$
4	KNEGHIJK	$\overline{KN}$	0.9	0.6	8.5	$T_{III}=8.5\pm0.4$
5	KEGHIJK	$\overline{KE}$	0.8	0.4	7.9	$T_{IV}=7.6\pm0.5$
6	KG′HIJK	$\overline{KG'}$	0.65	0.3	7.8	$T_V=6.2\pm0.4$
7	ABPE″A	$\overline{MN}$	1.3	1.2	14.4	$T_{VI}=3.65\pm0.15$

If we compare the calculated periods with those observed, we see that they are in good correspondence each other, as is shown in Fig. 5.

Fig. 5



A short-period seiche of from 1.6 to 1.8 minutes always accompanies one of from 3.6 to 3.8 minutes, so it seems the former is to be considered the over undulations of the transversal oscillation T_{VI}.

5. Note on Some Types of Seiche

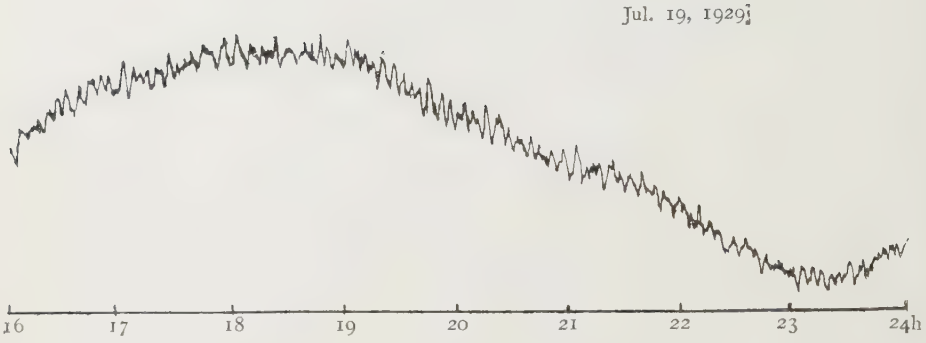
A type of conspicuous seiche is exemplified by an actual record in Fig. 6. Such seiches often occur continuously for several days, and show amplitudes within 10 cms. and periods from 1.6 to 1.8 minutes. They are always accompanied by typhoons.

If a typhoon appears far on the eastern sea of Formosa, our tide-guage immediately begins to record these seiches. When the typhoon has passed off Shiwono-misaki and gradually moved away northwards to the eastern sea of Sanriku or when it has gone over China or the Japan Sea, these seiches disappear.

Accordingly they occur mostly from Aug. till Nov. (see Fig. 3, light lines). Only two out of 46, the total number that have occurred in the past five years, are exceptional. These two cases were both when an unusual low-pressure of small area passed near Shiwono-misaki at a tolerable speed. The seiches of this type never occur with an ordinary low-pressure passing over the adjacent seas.

In this sense, we may say that such seiches forecast the visit of a typhoon.

Fig. 6



Next as to the seiches of very large amplitude, we usually meet them when a low-pressure passes over the adjacent seas and there can be distinguished two types among them. In one type, the amplitude increases gradually, and the other begins to oscillate suddenly with a large amplitude from the first.

Fig. 7 shows an example of the former, and Fig. 8 and Fig. 9 are examples of the latter.

According to the investigations of Mr. T. Namekawa and M. Takahashi, which will be published in the near future, the said kinds of seiches seem to be produced by minor fluctuations or kicks, but not the main depression of the atmospheric pressure and also not by wind.

Fig. 7

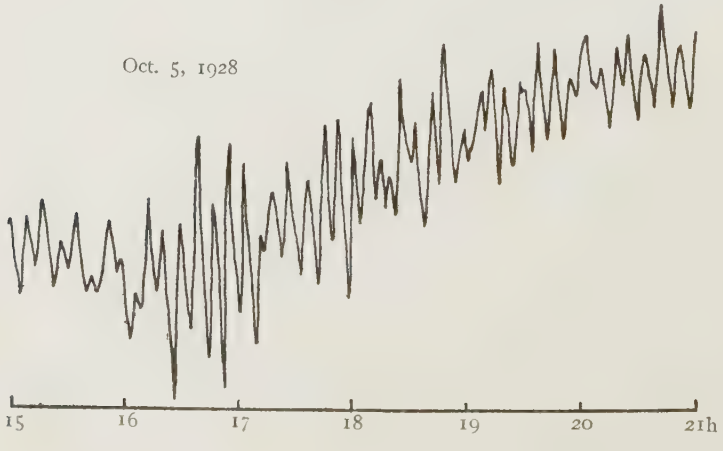


Fig. 8

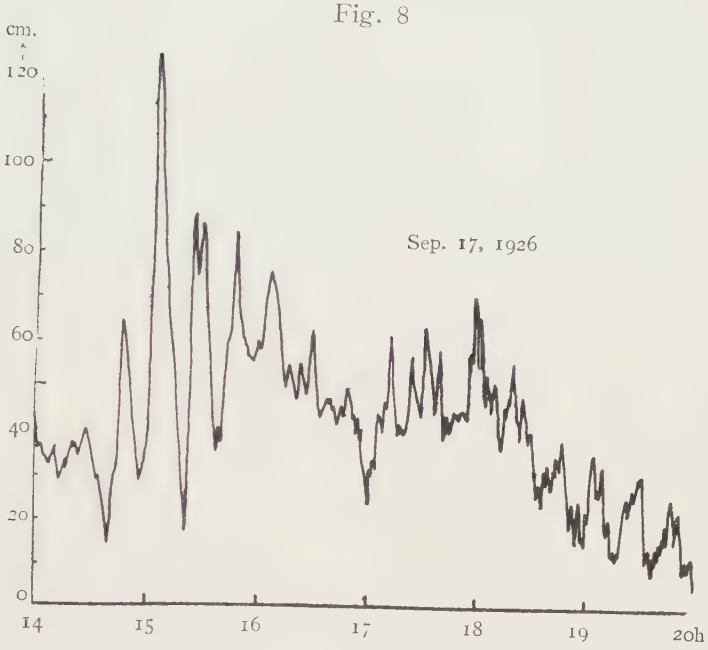
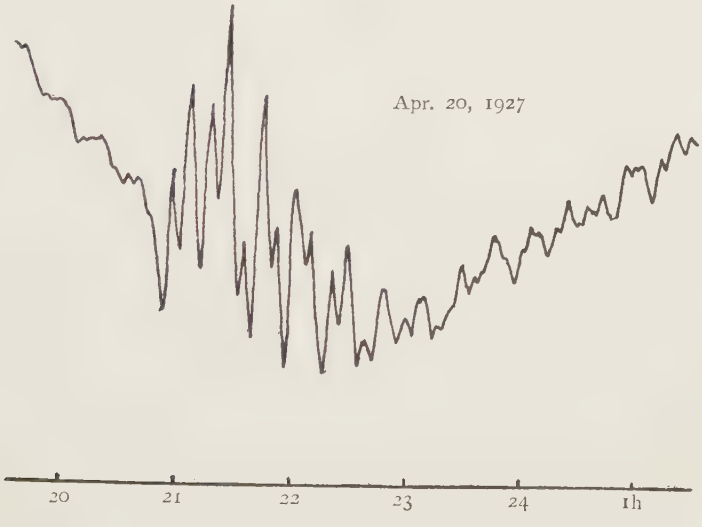

cm.
120
100
80
60
40
20
0
Sep. 17, 1926
14
15
16
17
18
19
20h

Fig. 9


Apr. 20, 1927
20
21
22
23
24
1h

We have had in recent years a great many earthquakes in the Kii Channel and its vicinity and can count more than one hundred perceptible earthquakes every year, but we have not yet detected any singularity in seiches that may be designated the effect of earthquakes.

In conclusion, the writer wishes to express his sincere thanks to Prof. T. Nomitsu for his kind guidance throughout the work, and also to the students for their laborious assistance in the numerical calculations.

Influence of Temperature upon the Diffusion Velocity of Solid Metals

(The Zinc-Copper System)

By

Chujiro Matano

(Received February 22, 1932)

Abstract

In the first part it is shown that the ratio of velocities of diffusion given by Weiss is equal to the ratio of coefficients of diffusion defined by Fick's law in the case of primary solid solutions. In the second part, the zinc-copper system being taken as an example, it is shown by means of an electrical resistance method that the velocity of diffusion can exist in the case of non-primary solid solutions and some of the states of diffusion have been examined by X-rays. In the third part it is proved that the relation between the velocity of diffusion V and the absolute temperature T is given by $V=Be^{-\frac{\alpha}{T}}$ instead of by Weiss' formula $V=Ke^{\beta T}$ with the zinc-copper system in the range of temperature 87–302° C, where B, K, α and β are constants and $\alpha=9.52\times10^3$ degrees.

Relation between Diffusion Velocity and Diffusion Coefficient

In the case of metals which do not form a perfect solid solution, we can easily see from the complexity of their equilibrium diagrams that there is no such constant as the coefficient of diffusion which is independent of the concentration and time. Nevertheless, H. Weiss[1] has found by microscopic examination that when samples which are both composed of the two kinds of metals to be tested, are heated at different temperatures, T and T', and one of them reaches a certain state (say A) after the time interval t_1 and another state (say B) after t_2, then the other of them also reaches the state A after the time

1. H. Weiss: Ann. de Chimie, **19**, 21 (1923); and **20**, 131 (1923).

interval t_1' (which is different from t_1) and the state B after t_2', and, moreover, there exists the relation

$$t_1/t_1' = t_2/t_2'. \qquad (1)$$

Since the states A and B are arbitrary, the above ratio is constant in any state, and may be put as V'/V (V corresponding to T and V' to T'). Weiss called V the velocity of diffusion at the temperature T.

Now we will consider what meaning the velocity of diffusion has in the case where there exists the coefficient of diffusion D which is defined by Fick's law[1] or by its form of differential equation

$$\frac{\partial c}{\partial t} = D\Delta c,$$

where c is the concentration, t the time and Δ the Laplace operator. The concentration, then, will be given by the form $c=f(Dt, x, y, z)$, where x, y and z are the space coordinates which determine the point where the concentration is considered, and f is a certain function[2] which is determined if the boundary and initial conditions are given. If we choose, as in Weiss' case, the same two samples and heat one at the temperature T and the other at T', then the first state is reached after the times t_1 and t_1' and the other state is reached after t_2 and t_2'. In order to get the same state at the different temperatures and different intervals of time, the following relations must exist:—

$$c=f(Dt_1, x, y, z)=f(D't_1', x, y, z),$$

and $$c=f(Dt_2, x, y, z)=f(D't_2', x, y, z),$$

or $$Dt_1=D't_1' \quad \text{and} \quad Dt_2=D't_2',$$

and so $$D'/D=t_1/t_1'=t_2/t_2', \qquad (2)$$

where D and D' are the coefficients of diffusion referring to the temperatures T and T' respectively. Comparing this with (1), we have

$$D'/D=V'/V, \qquad (3)$$

i. e. the ratio of the coefficients of diffusion defined by Fick's law at any two temperatures is the same as the ratio of the velocities of

1. Fick: Pogg. Ann., **94**, 59 (1855).
2. Riemann-Weber: Differentialgleichungen der Physik II S. 177 (1927).

diffusion defined by Weiss at those temperatures in the case of solid solutions.

Determination of Diffusion Velocity by Resistance Method

General consideration of the method: Weiss[1] has determined the velocity of diffusion of various metals and N. W. Ageew and O. I. Vher[2] have determined that of aluminium and iron by microscopic means, but the velocity of diffusion can be determined from the change in the electrical resistance of the samples examined. As in the previous experiment[3] carried out in the case of primary solid solutions, take two samples made of two kinds of metals in the form of foils, and heat them at the different temperatures T and T', then measure the electrical resistance of them at the same temperature T' $(<T)$. The concentration c of the one metal will be given by $c=f(x, t)$ at T, and $c=\varphi(x, t)$ at T', where f and φ are unknown functions, t the time, and x the space coordinate which is perpendicular to the flat surface of the sample. If the same state be reached at the times t and t' in the respective cases as Weiss supposed, then the relation $c=f(x, t)=\varphi(x, t')$ must exist and the electrical resistance of the samples has also the same value. Conversely, if the resistance of many kinds of samples of the same pair of metals be measured, and the time intervals which are necessary to bring the resistance to the same value be compared, and if the series of time ratios have a constant value in each case, we can say that Weiss' conception is correct and the velocity of diffusion exists.

To illustrate this method the author has chosen the system of zinc and copper, although the diffusion phenomena of this system have already been studied by Weiss[4] and S. L. Hoyt[5] by microscopic examination and by C. F. Elam[6] by the X-ray method with large single-crystals of copper, but in any case the velocity of diffusion has not yet been given.

Production of samples, method of measurement and apparatus:

1. H. Weiss, loc. cit.
2. N. W. Ageew and O. I. Vher: Jour. Inst. Metals, **44**, 83 (1931).
3. C. Matano: These Memoirs, **14**, 123 (1931).
4. H. Weiss, loc. cit.
5. S. L. Hoyt: Amer. Inst. Min. Met. Eng. Tech. Publ., **128**, 1 (1928).
6. C. F. Elam: Jour. Inst. Metals. **43**, 217 (1931).

As in the previous paper[1] the samples were made in the form of foils by alternate electroplating with copper and zinc. A wax surface covered with graphite was first plated with copper in the electroplating solution; 100 c.c. of water containing 4.35 gms. of caustic soda, 2.60 gms. of copper sulphate and 13.00 gms. of Rochelle salt. Then zinc and copper layers were added alternately, but as the above solution used for copper was not suitable for zinc objects, the following solutions were used: for zinc, 100 c.c. of water containing 2.20 gms. of sodium citrate and 3.52 gms. of zinc chloride; and for copper, 100 c.c. of water containing 2.12 gms. of sodium bisulphite, 1.75 gms. of copper acetate and 2.12 gms. of potassium cyanide. After a suitable thickness had been obtained, the foils were peeled off and cut into strips about 0.1 cm. in breadth and 15 cms. in length. The time for each plating, the current density, the number of layers and the total thickness of the foils are tabulated in Table I.

Table I

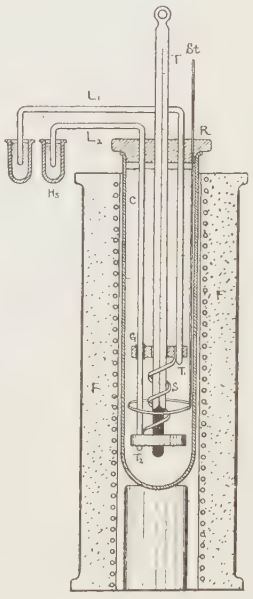
Foil	Time for plating each half layer mins.	Current Density m. amp./cm^2.	Number of Layers	Total Thickness cm.$\times 10^{-3}$	Thickness of each layer cm.$\times 10^{-4}$
I	Cu 40 Zn 10	3.5 6.7	8	3	4
II	Cu 80 Zn 20	3.5 7.5	4	3	8
III	Cu 180 Zn 15	3.5 6.7	2	5	25

The sample, held in the terminals as described below, was then put in a vacuum or in glycerin or castor oil which were heated by the electrical resistance furnace, and the electrical resistance of it was measured by the null method with a Wheatstone bridge made by Hartmann and Braun. The terminals are shown in Fig. 1. L_1 and L_2 are the copper lead wires whose resistance is about 0.003 ohm, and T_1 and T_2 are the brass terminals at which the sample S is fixed by screws. T is an ordinary mercury thermometer measuring up to 360°C, C the castor oil which is contained in the glass vessel, R the rubber stopper and F the electrical resistance furnace. G is a glass tube which insulates the lead wire L_2 from the terminal T_1. Hs are glass vessels filled with mercury and at these parts the lead wires

1. S. Tanaka and C. Matano: These Memoirs, **13**, 343 (1930).

which are connected to the terminals of the Wheatstone bridge are in contact with the lead wires L_1 and L_2. St is a stirrer.

Fig. 1



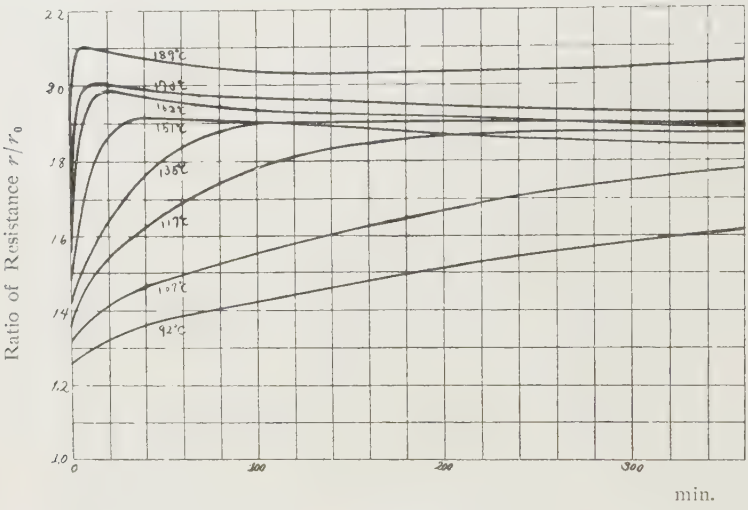
From the theoretical point of view, it is best to heat the sample in a vacuum, but since the diffusion occurs very fast in some cases and although the sample and terminals have only small heat capacities, a sufficiently long duration is necessary before the sample etc. are brought to the fixed constant temperature, so the author, in many cases, rather heated the sample in some insulating liquid with such a large heat capacity that the sample (owing to the good thermal conductivity of it) reached the constant temperature of the liquid in an instant when it was put in the liquid. The lead wires are sufficiently thick so that the change of resistance owing to the change of temperature is negligible. The sample S is spiraled near the mercury in the thermometer and the temperature can be measured accurately. No effect of thermoelectricity can be detected by reversing the direction of the current in the sample when the resistance is measured.

In order to lower the temperature of the sample heated at T to $T'(<T)$ quickly, the electrical furnace was opened and the vessel was exposed to the air. The resistance of the sample at T' was measured and to elevate the temperature of the sample to T quickly, a large amount of current was sent through the furnace. But it required a fairly long time and this point is the chief drawback in this method.

Results of experiments, existence of diffusion phenomena: The results are shown in the curves in Fig. 2. The abscissa is the time interval which is measured from the instant when the sample is put in the furnace and so when the diffusion begins. The ordinate is the ratio of the resistance at the temperature and the time selected to the resistance at $15^\circ C.$ where diffusion does not occur appreciably over a long time. The thickness of the sample or rather the thickness of each layer plays an important part in every problem of diffusion and so in this case by taking the ratio of the resistances, the effect due to the difference in the length and the breadth of each sample has been removed.

In every curve the resistance changes as the time passes and this shows that diffusion has taken place. The resistance first increases, then reaches the maximum value and finally decreases, and as every curve is of this nature, there seems to exsist such a quantity as that

Fig. 2



called "the velocity of diffusion". We understand that the part where the resistance increases rapidly also shows the vigorous occurrence of diffusion. But in the part where the resistance decreases slowly, we can not so easily determine whether this effect is due to diffusion or to annealing, which effect the author considers as due to the phenomena of grain growth etc. To confirm this point, X-ray photographs were taken with the Debye-Scherrer camera in the Müller spectrograph, but instead of the pin hole, the slit was used. The Shearer metal tube was used as the X-ray apparatus and the current strength was about 3 milliamp., the maximum voltage applied was 60 K. V. and the time of exposure was 7 hours in each case. Three photographs taken with the samples from foil I are shown in Plate I. The first was obtained with the sample before heating and is shown in Fig. 1a; the second was taken with a sample kept at 165°*C.* for 26 minutes, when its resistance is at its maximum value, and then quenched, and is shown in Fig. 1b; and the third was obtained with a sample kept at 165°*C.* for over 350 minutes, when the resistance is considerably less than the maximum value, and also quenched, and is shown in Fig. 1c. From these photographs we can say that the

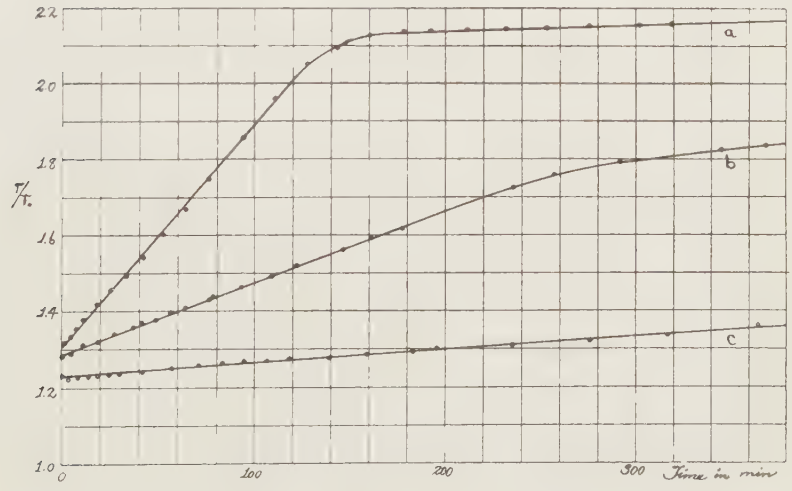
three stages are different from each other, and while the diffusion occurs in the interval when the resistance increases, it also occurs in the interval when the resistance decreases, and as neither broadening of spectral lines nor aggregation of Laue spots can be detected in Fig. 1c, the grain growth has not occurred yet.

Existence of diffusion velocity: The existence of velocity of diffusion was examined as follows:— A sample obtained from foil II was first heated to 149°*C.*, and its resistance was measured at that temperature, the result being shown in Fig. 3a. Another sample from the same foil was heated to 131°*C.* and its resistance was measured at that temperature with the results shown in Figs. 3b and 4c; the resistance of another sample at 108°*C.* is shown in Fig 3c. Still another sample from the same foil was heated to 149°*C.* and its resistance was measured at that temperature (results shown in Fig. 4a) and also at 131°*C.* (result in Fig. 4b).

As has been mentioned in the preceding section, it is difficult to lower the temperature and again raise it to the previous temperature instanteneously, and in this experiment it took some five minutes to do this.

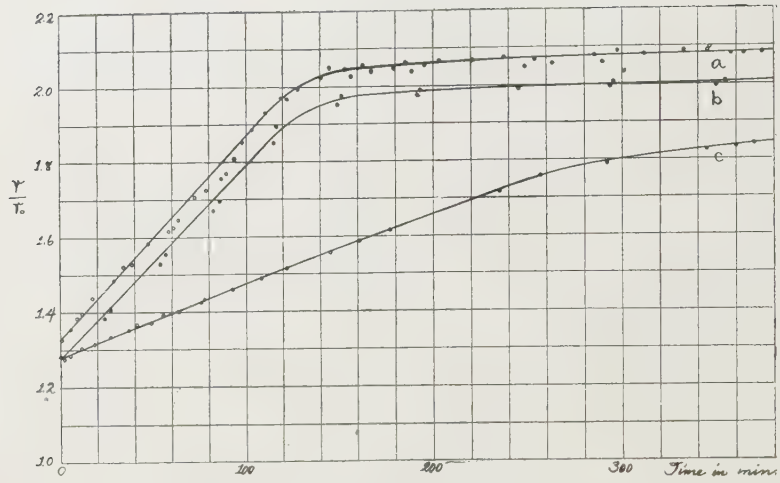
On comparing the curves of Figs. 3a and 4a, the points which

Fig. 3



a. Heated at 149°*C* and measured at 149°*C*
b. „ 131°*C* „ 131°*C*
c. „ 108°*C* „ 108°*C*

Fig. 4



a. Heated at 149° *C* and measured at 149° *C*
b. „ 149° *C* „ 131° *C*
c. „ 131° *C* „ 131° *C*

determine the curve Fig. 4a are somewhat disorderly, but we can say that both curves have the same form, i. e. both curves are at first nearly straight and their slopes to the time axis are 5.5×10^{-3}, and 5.2×10^{-3} min.$^{-1}$ respectively; at about 140 minutes, the curves are somewhat flattened and afterwards both curves are again nearly straight and their slopes in this time take the same value, 1.25×10^{-4} min.$^{-1}$ From this fact, it is clear that the diffusion phenomenon was nearly the same whether the sample was heated at the constant temperature or heated at the constant temperature but disturbed many times by lowering its temperature for small intervals of time. On comparing the curves in Figs. 4a and 4b, we see that both curves again have the same form in many respects, viz. the inclination of the straight portion, the point where the line changes its direction, but the curve in Fig. 4a is always higher than the curve of Fig. 4b, nearly the same distance from it throughout the whole interval of the measurement. From this last fact, it is evident that the direction of the curve of Fig. 4a can be taken instead of that of Fig. 4b, if the direction of a curve of the nature of that in Fig. 4b is needed. This fact will be utilised in the latter part of this paper. Lastly, on comparing the curves in Figs. 4b and 4c, we see that both curves start from nearly the same point, and run in straight lines but have different slopes;

while the one tends to change its direction at nearly 100 minutes, the other does so at nearly 260 minutes, and as the one tends to change its direction sharply, the other does so very slowly. From these facts, it is clear that in the straight portion in the early stage where the diffusion occurs vigorously, the velocity of diffusion exists strictly, as the ratio of the velocities of diffusion at these temperatures can be given from the ratio of their slopes and this is independent of time, and so independent of the homogenisation of the component metals. The details of this are as follows:

The equation of the curve in Fig. 4b is

$$r/r_0 = 1.28 + 5.1 \times 10^{-3} t \qquad (0 \leqq t \leqq 100)$$

and the equation of the curve in Fig. 4c is

$$r/r_0 = 1.28 + 1.9 \times 10^{-3} t \qquad (0 \leqq t \leqq 260)$$

graphically, where r is the resistance at the time t, which is expressed in minutes, and r_0 is the resistance at time $t=0$ at the temperature $15^\circ C$. Since the state of diffusion is the same when the resistance is the same, so is in the same state in the above equations, let the two time intervals which are necessary to bring them to that state be t_{149} and t_{131}, then

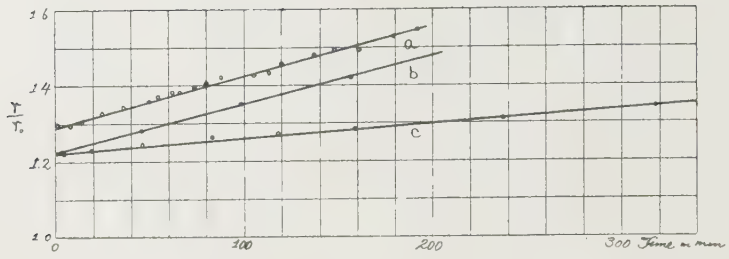
$$t_{149}/t_{131} = 1.9/5.1 = 0.37 \quad (= V_{131}/V_{149}),$$

where t_{149} is the time required for the sample heated to $149^\circ C$. and t_{131} is for that heated to $131^\circ C$., and this is the ratio of the velocities of diffusion V_{131}/V_{149}.

After the straight portion stage, the direction of the curve is not independent of time, but from the similarity of the curves of Figs. 4b and 4c, even in this part, broadly speaking, the velocity of diffusion exists. The points where the direction tends to change give the ratio of the velocities as $100/260 = 0.39$ and this ratio nearly coincides with the ratio 0.37 given above.

To take another example—the sample obtained from foil II was heated to $108^\circ C$. and its resistance was measured at that temperature, with the results shown in Fig. 5c. Next another sample from the same foil was heated to $131^\circ C$. and its resistance was measured at $131^\circ C$. and occasionaly at $108^\circ C$. by lowering the temperature to that point in a small time interval (about 15 minutes). The results are shown in Figs. 5a and 5b. As in the above example, comparing the curves in Figs. 5a and 4c, we see that both curves are nearly straight in the interval of time when the measurement was made, but the

Fig. 5



a. Heated at 131°*C* and measured at 131°*C*
b. „ 131°*C* „ 108°*C*
c. „ 108°*C* „ 108°*C*

slopes are different, the curve in Fig. 4c being more inclined than the curve in Fig. 5a. This fact, however, may be explained as follows: The time interval which is needed to lower the temperature from 131°*C.* to 108°*C.* is so long that the diffusion occurred in this interval at a temperature below 131°*C.* Next, comparing the curves in Figs. 5a and 5b, we see that the two curves have the same slope as in the former example and the explanation must be the same. Lastly, comparing the curves in Figs. 5b and 5c, we see that they are also of the same nature as that of the former example. And in this case, also, the velocity of diffusion exists strictly.

The equations of the curves in Figs. 5b and 5c are

$$r'/r_0 = 1.223 + 1.27 \times 10^{-3}t$$

and

$$r/r_0 = 1.223 + 3.74 \times 10^{-4}t$$

graphically. So the ratio of the velocities of diffusion, which is the ratio of the slopes is

$$t_{131}/t_{108} = 3.74/12.7 = 0.273 \ (= V_{108}/V_{131}).$$

Relation between Diffusion Velocity and Temperature

Determination of ratio of diffusion velocities at various temperatures: In the preceding section it is shown that the velocity of diffusion exists and the ratio of the velocities at two different temperatures can be determined from the ratio of the times which are necessary to bring the samples to the same value of resistance taken as a standard, the portion of the resistance due to the temperature coefficient being removed. But in general it is difficult experimentally to remove the portion of the resistance due to the temperature

coefficient. In the case of the samples from foil II, the resistance-time curve has a straight line portion and what is needed to determine the ratio in question is the ratio of the slopes, and so from the results described in the preceding section, the slope of the straight line can be used in the resistance-time curve in which the resistance was measured at the temperature at which the diffusion has occurred and the resistance due to the temperature coefficient has not been removed. The above method can be utilised for the samples from foil III. Since the ratio of the slopes is equal to the ratio of the velocities of diffusion, the slope is itself proportional to the velocity of diffusion

Table II

Foil II		Foil III	
Absolute Temp.	Slope of Curve, min.$^{-1}$	Absolute Temp.	Slope of Curve, min.$^{-1}$
361	1.65×10^{-4}	453	7.16×10^{-3}
366	1.8×10^{-4}	478	1.34×10^{-2}
381	3.6×10^{-4}	497	3.03×10^{-2}
404	1.27×10^{-2} *	511	4.23×10^{-2}
	1.8×10^{-3} *	531	1.11×10^{-1}
422	5.1×10^{-3} *	546	1.62×10^{-1}
	5.5×10^{-3} *	575	4.20×10^{-1}
440	1.7×10^{-2}		
462	4.5×10^{-2}		
488	1.3×10^{-1}		

* See Figs. 5 and 4.

Table III

Foil I	
Absolute Temp.	t_m min.
408	120
424	44
435	21
446	14
462	7

and the constant of this ratio is the same when the temperature is varied, if only the samples are of the same kind. The slopes of the lines are shown in Table II.

Now, in the case of the curves in Fig. 2, there is no straight line portion, and since any state can be taken as a standard, it is very satisfactory to find that there is a corresponding point on each curve, if a special position, such as the point where the resistance is maximum, be taken as a standard. For there are many reasons for considering that the point where the resistance is maximum corresponds at each temperature, since the resistance-concentration curves have nearly the same aspect within a moderate range of temperature. The ratio of the velocities of diffusion can thus be measured. The results obtained with the samples from foil I are shown in Table III. t_m, the time interval which is required for the samples to attain the maximum resistance, is inversely proportional to the velocity of diffusion.

Formulae which express the relation between diffusion velocity and temperature: The empirical formula which combines temperature and the velocity of diffusion given by Weiss[1] is

$$V = 1/t = K(e^{\beta T} - 1),$$

where V is the velocity of diffusion, t the time interval which is necessary to bring the sample to a certain state of diffusion, K and β constants independent of temperature, e the base of natural logarithms and T the absolute temperature. But usually 1 is small in comparison with the first term in the brackets and can be neglected, so the above formula becomes

$$V = Ke^{\beta T}. \qquad (4)$$

Any state can be taken as a standard; only the ratio of the velocities of diffusion has an important meaning and so K is not important and what is important is β.

In the case where the coefficient of diffusion exists, first S. Dushman and I. Langmuir[2] and afterwards J. Frenkel[3] and others deduced from the theoretical consideration the following formula,

$$D = Ae^{-\frac{\alpha}{T}}, \qquad (5)$$

where D is the coefficient of diffusion, A that of $T \to \infty$, α the constant, e the base of natural logarithms and T the absolute temperature. This formula was confirmed experimentally by many investigators[4] in the case of solid solutions, although the results of A. Obrutsheva and G. Hevesy's experiments[5] on the self diffusion of lead have confirmed rather the formula with two similar terms derived by A. Smekal[6].

Now between the coefficient of diffusion and the velocity of diffusion there exists the relation (3) in the case of solid solutions and so from (5) there must be the relation

$$V = Be^{-\frac{\alpha}{T}}, \qquad (6)$$

where B is a constant independent of temperature, and depending upon the state of diffusion which is taken as a standard. In the case

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1. H. Weiss, loc. cit.
2. S. Dushman and I. Langmuir: Phys. Rev., **20**, 113 (1922).
3. J. Frenkel: Zeits. f. Phys., **35**, 652 (1926).
4. H. Braune: Zeits. phys. Chem., **110**, 147 (1924); W. Jost: Zeits. phys. Chem., **9**, 73 (1930); C. Matano, loc. cit.
5. A. Obrutsheva and G. v. Hevesy: Nature, **115**, 674 (1925).
6. A. Smekal: Zeits. f. Electrochem., **34**, 472 (1928).

of non solid solutions, in some cases[1] formula (4) does not express the results of experiments exactly, so we shall consider whether formula (4) or (6) expresses the result of this experiment more satisfactorily.

Let the quantity which is proportional to the velocity of diffusion V, such as the slope or the reciprocal of t_m, be U, then $V=U/C$, where C is a constant; and from (4) taking logarithms we have

$$\log_{10}U=\log_{10}V+\log_{10}C=\log_{10}K+\beta\cdot\log_{10}e\cdot T+\log_{10}C$$
$$=\text{const.}+\beta\cdot\log_{10}e\cdot T, \qquad (7)$$

and from (6) we have

$$\log_{10}U=\text{const.}-(\alpha\cdot\log_{10}e)/T. \qquad (8)$$

Plot the curve as $\log_{10}U$ in one coordinate and T or $1/T$ in the other coordinate on a graph using the results shown in Tables II and III. Then in each case the curve seems to be a straight line and both formulae (7) and (8), and consequently (4) and (6) seem to express the results nearly satisfactorily in the range of temperatures at which the measurement is carried out for each sample of the same kind. The slope of the line determines the constants, the values of which are summarized in Table IV.

Table IV

Foil	$\beta\cdot\log_{10}e$ $(\text{degrees})^{-1}\times10^{-2}$	$\alpha\cdot\log_{10}e$ $\text{degrees}\times10^{3}$	Range of Temperature
I	2.3	4.3	408–462
II	2.4	4.3	361–488
III	1.8	4.1	453–575

α and β must not depend on the kind of the foils or in other words these are constants which depend only upon the nature of the metals in which the diffusion occurs. In this sense it seems from Table IV that formula (6) expresses the results more satisfactorily. To show this more clearly, the following curves will be drawn: Since what is important is α or β and not the initial value of the straight line, we will shift the line to its proper place by moving the temperature axis upwards or downwards and plot the curve in one figure, then the curves in Figs. 6 and 7 will be obtained. In these figures it is clear

1. N. W. Ageew and O. I. Vher, loc. cit.

Fig. 6

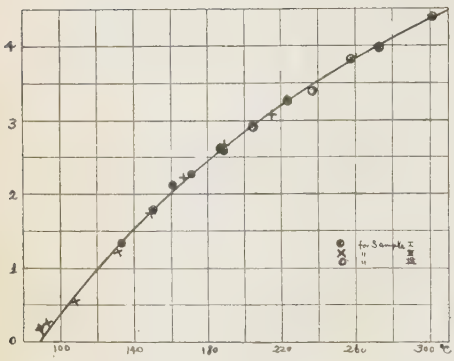
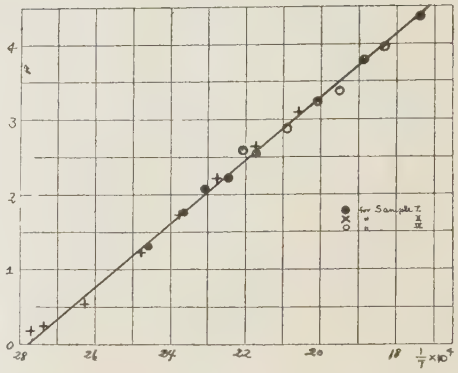


Fig. 7



that the curve corresponding to formula (6) is much straighter than the curve corresponding to formula (4) which deviates systematically from a straight line. From this a can be determined graphically and is equal to 9.52×10^3 degrees in the range of temperature $87 - 302^\circ C$. (Weiss' result with the tin-copper system gives $\beta \cdot \log_{10} e = 1.6 \times 10^{-2}$ per degree, which value is comparable to the above results in Table IV with the zinc-copper system).

The conclusion is as follows: The formulae $V = Be^{-\frac{\alpha}{T}}$ and $V = Ke^{\beta T}$ both represent nearly the experimental facts, but strictly speaking, the former expresses the results more satisfactorily in the range of temperature $87 - 302^\circ C$. with the zinc-copper system. The constant a is equal to 9.52×10^3 degrees in this case.

In conclusion the author wishes to express his hearty thanks to Prof. M. Ishino and Prof. U. Yoshida of Kyoto Imperial University and to Prof. S. Tanaka of Osaka University of Engineering for their kind guidance. The author also wishes to express his sincere thanks to Mr. T. Asada of the Shiomi Institute for his kind permission to read the periodicals which were needed to accomplish this work.

Physical Laboratory,
The Osaka University of Engineering.

Plate I

Fig. 1 a

Fig. 1 b

Fig. 1 c

On the Splitting of the Sulphonic Group from the Aromatic Ring by Electrolytic Reduction

By

Motooki Matsui and Gisho Sakurada

(Received February 24, 1932)

Some of the sulphonic groups attached to the aromatic ring can easily be removed by electrolytic reduction. For instance, o-sulphobenzoic amide was recently found in our laboratory[1] to undergo reduction electrolytically in an alkaline solution and produce benzamide with a yield of 65%. The facility with which the sulphonic group is thus split from the aromatic ring seems to be governed by the nature of the aromatic ring itself, and also by the properties and position of other radicals attaching to the ring. According to Friedländer and Lucht[2] α-naphthalene sulphonic acid is reduced with sodium amalgam more easily than the corresponding β-compound. Some such points or even more minute ones may perhaps be investigated electro-chemically. As to electrolytic reduction, however, the works dealing with this subject are very scanty; the only instance we can find in chemical literature is that of the German patents[3] concerned in the process used for the elimination of some sulphonic radical from a polysulphonic compound.

In the research here reported, it was found that, the presence of an acidic radical such as COOH favours the splitting of the sulphonic radical in a benzene ring, while a basic radical like NH_2 acts contrarily. And even the influence of one and the same radical is not always the same, but is greatly altered by difference in the relative position of it and the sulphonic radical. In reduction of sulphobenzoic acids,

1. These Memoirs, series A, **15**, 155 (1932)
2. Ber., **26**, 3028 (1893).
3. D. R. P., 248527, 255724.

the o- and p-compounds are reduced with far greater ease than the corresponding m-compound, but in the case of sulphanilic acids, the m-compound is far more readily reduced than the p-compound.

All the reduction experiments described below were carried out with the lead cathode; the use of mercury instead of lead did not show much difference.

Exmerimental

In all the experiments here described, caustic soda solutions were always used as the catholyte, to which sometimes alcohol was added to increase the solubility of the sulphocompound used for reduction. As the anolyte, a concentrated sodium carbonate solution was taken, and electrolysed with electrodes of lead.

1. Benzenesulphonic acid

Three grams of the sodium salt were dissolved in 100 c.c. of 20% caustic soda solution, and the solution was electrolysed by passing a current of 2.4 amperes/60 sq. cms. at 25°. Shortly after the electrolysis commenced, benzene began to be evolved at the cathode, and at the same time the presence of sulphurous acid in the catholyte became recognizable. During the electrolysis, 5 c.c. of the cathode solution was taken out at intervals of an hour, and the amount of sulphurous acid was determined iodometrically in order to find how far the sulphonic acid had been reduced.

Time of electrolysis (Hours)	SO_2 (mg.)	Amount reduced (%)
2	18.8	35
3	20.4	38
4	20.9	39
5	20.9	39

The reduction was thus observed to have practically ended after 3 hours' electrolysis.

Influence of temperature.—Under exactly the same conditions as described above, another series of four experiments was made, a current of 4 amperes/sq. dm. being passed for 3 hours at different temperatures.

Temperature	Amount reduced (%)
15°	60
25°	39
55°	10
65°	4

The results show that high temperature has a deleterious effect on the reduction.

Influence of the current density.—Electrolysis was next conducted with currents of different density passed for 3 hours. The results were as follows:

Current density (amp./sq. dm.)	Conc. of NaOH (%)	Temp.	Amount reduced (%)
1.6—2.0	10	20°	trace
2.2	„	„	2.5
4.0	„	„	6.5
2.0	20	15°	6.8
2.5	„	„	25.0
4.0	„	„	60.0

High current density is thus seen to favour the reduction.

Influence of the concentration of alkali.—Caustic soda solutions of different degrees of dilution, in which 3 grams of benzene sulphonic acid were dissolved, were electrolysed.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Amount reduced (%)
5	6.0	2.4
10	4.0	6.3
20	4.0	39.0

From the above results so far described it became clear that high concentration of alkali, greater density of the current and low temperature are essential for electrolytic reduction of benzene sulphonic acid.

2. Sulphanilic acid

Electrolysis of sulphanilic acid was carried out under nearly the same conditions as in the case of benzene sulphonic acid, but no appreciable reduction could be observed.

3. Metasulphanilic acid

Two grams of the crystalline acid were dissolved in 100 c.c. of 5–20% caustic soda solution, and other conditions being kept nearly the same as in the case of benzene sulphonic acid, electrolysis was carried out. The results were as follows:

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2.0	21°	7	0
10	3.0	50°–70°	„	0
„	4.0	25°	4	26.0
20	„	„	2	37.0

For reduction of metasulphanilic acid high concentration of alkali and also high current density are essential conditions of electrolysis.

4. Paraphenolsulphonic acid

This acid could not be reduced electrolytically.

5. Orthosulphobenzoic acid

Three grams of the crystalline acid were dissolved in 100 c.c. of caustic soda solution of different concentrations, and the amounts of benzoic acid formed by the electrolysis were estimated. As is seen in the following table, low temperature was found to be the most important condition for this electrolysis.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
2	2.0	19°	4	59
5	„	„	6	77
„	„	55°–63°	5.5	56
10	3.0	22°	5	63

6. Metasulphobenzoic acid

Two grams of sodium metasulphobenzoate were electrolytically reduced in caustic soda solution, and the amounts of benzoic acid formed were determined with the following results:

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2.0	10°	2	37
"	"	25°	"	"
"	"	62°	"	21
"	4.0	25°	1.5	38
10	"	"	2	36

Reduction of m-sulphobenzoic acid also depends chiefly on temperature, and is not much affected by either concentration of alkali or current density, if the temperature is kept below 25°.

7. Parasulphobenzoic acid

The sodium salt of this acid was electrolysed in the caustic soda solution with the following results:

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2	25°	2	77
"	4	62°	"	74
10	4	25°	"	77

High temperature tends to lower the reduction efficiency somewhat.

8. α-Naphthalenesulphonic acid

Electrolysis was sometimes conducted with the alcoholic caustic soda solution, as the sodium sulphonate is soluble only with difficulty in a concentrated caustic soda solution. After about 15 minutes'

Catholyte			Current density (Amp./sq. dm.)	Temp.	Amount reduced (%)
NaOH (g.)	H_2O (c.c.)	C_2H_5OH (c.c.)			
—	100	—	1.7	20°	3.8
5	90	10	2.0	15°	8
"	"	"	2.5	45°	23
"	100	—	4.0	25°	17
5	100	—	4.0	50°	39
10	70	30	2.5	35°	23
"	80	20	4.0	25°	38
"	"	"	"	55°	52
"	"	"	5.0	25°	36

electrolysis naphthalene began to separate out. To prevent loss of naphthalene by volatilization, a round-bottomed flask containing cold water was placed on the cylindrical cell which was used as the cathode compartment. The amount of the acid reduced was calculated from that of sulphurous acid determined iodometrically.

Unlike the case of reduction of benzene sulphonic acid and sulphobenzoic acid, high temperature favours the reduction of α-naphthalenesulphonic acid.

9. β-Naphthalenesulphonic acid

The sodium salt of the sulphonic acid was electrolysed in exactly the same manner as in the case of the corresponding α-compound; the results were as follows:

Catholyte			Current density	Temp.	Amount reduced
NaOH (g.)	H_2O (c.c.)	C_2H_5OH (c.c.)	(amp./sq. dm.)		(%)
—	100	—	1.4—2.0	15°	3.8
5	75	25	1.4	„	6.2
„	100	—	4.0	25°	11.1
„	„	—	„	50°	5.7
„	65	35	2.8	20°	3.0
10	50	50	1.4	15°	3.8
„	„	„	2.5	50°	3.8
„	70	„	4.0	25°	14.0

When compared with the α-compound reduction of β-naphthalenesulphonic acid is far more difficult than that of the α-compound, and is somewhat retarded or at least not promoted by high temperature.

10. Naphtholsulphonic acids

Of the naphtholsulphonic acids such as 1 : 2, 1 : 4, 1 : 5 and 2 : 6, only 1 : 4 and 1 : 5 could be reduced, with a yield of about 10% of α-naphthol, by passing a current of 4 amperes/sq. dm. into 10% caustic soda solution; the 1 : 2 and 2 : 6 acids remained quite unaffected. In electrolysis of disulphonic acids though slight formation of sulphurous acid could be perceived, yet not even a trace of the reduction product was procured.

11. Naphtionic acid

Sodium naphtionate was electrolysed in the caustic soda solution for 4 hours. After the electrolysis was over, the *α*-naphthylamine separated out from the catholyte and also that remaining in the dissolved state were collected and weighed. As a result, naphtionic acid was found to undergo reduction comparatively well, especially when a current of high density was applied, thus—

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Yield of α-naphthylamine (%)
3	1.4	20°	trace
10	2.0	25°	21
„	4.0	„	72
„	„	60°	81

12. Naphthylaminesulphonic acid 1 : 5

Reduction of this acid in the caustic soda solution was found to proceed rather smoothly at high temperature, thus—

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Acid reduced (%)
10	2.5	18°	4	6
„	„	65°	„	73

13. Cleve's salt

A mixture of naphthylaminesulphonic acids 1 : 6 and 1 : 7, known as Cleve's salt, could not be reduced.

14. Naphthylaminesulphonic acid 2 : 5

After electrolysing the caustic soda solution of the acid for 2.5 hours the catholyte was nearly neutralised with hydrochloric acid, and the slightly alkaline solution thus formed was distilled with superheated steam, when *β*-naphthylamine melting at 106° was obtained as scaly crystals.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Amount reduced (%)
5	4.0	40°—45°	12
10	„	16°	„

15. Naphthylaminesulphonic acid 2 : 6

After electrolysis the presence of sulphurous acid in the catholyte could be detected, but the amount of β-naphthylamine produced by reduction was so small that its determination was impracticable.

16. Amidonaphtholsulphonic acids

Monosulphonic acid 2 : 6 : 8 and disulphonic acid 1 : 8 : 3 : 6 were subjected to electrolysis, but no recognizable reduction took place.

Electrolysis of a Mixture of Two Fatty Acids

By

Motooki Matsui and **Shingo Arakawa**

(Received March 7, 1932)

Kolbe's reaction, which various fatty acids undergo on electrolysis, is not always the same, even when the electrolysis is conducted under exactly the same conditions; some produce a saturated hydrocarbon such as methane or ethane, and others an unsaturated one like ethylene, and not seldom alcohols and esters are formed instead of hydrocarbons. Whether the anodic reactions which give rise to these different products fundamentally differ from each other, or whether the reaction which primarily takes place at the anode is always the same but the products of the primary reaction undergo secondary reactions in many different ways is still an unsettled problem.

In the hope of contributing to the solution of this problem, authors took up the study of the electrolysis of two fatty acids mixed together. The idea was as follows: If propylene, which is the main product of electrolysis of propionic acid, is the substance primarily formed anodically, the existence of the ethyl radical in considerable concentration at the anode cannot be imagined, and as a consequence, the reaction in which the ethyl radical may be regarded to have taken part will never be expected to occur in that electrolysis. Nevertheless, as is described in the experimental part of this report, when propionic acid was electrolysed together with a higher fatty acid such as palmitic or stearic acid, a new hydrocarbon consisting of the alkyl radicals of both fatty acids is produced, besides the hydrocarbons formed in the electrolysis of each individual acid. Moreover, the molecular proportion of two hydrocarbons $C_{17}H_{36}$ and $C_{30}H_{62}$ formed from a mixture of propionic acid and palmitic acid was nearly the same as that of two hydrocarbons $C_{16}H_{34}$ and $C_{30}H_{62}$ produced from a mixture of acetic acid and palmitic acid, as is seen in the following table:—

Acid	Molecular proportion, taken	Hydrocarbon
CH_3CO_2H $C_{15}H_{31}CO_2H$	1.5 : 1	$C_{16}H_{34}$ (1.3 : 1) $C_{30}H_{62}$
CH_3CO_2H $C_{17}H_{35}CO_2H$	1.5 : 1	$C_{18}H_{38}$ (1.5 : 1) $C_{34}H_{70}$
$C_2H_3CO_2H$ $C_{15}H_{31}CO_2H$	1.5 : 1	$C_{17}H_{36}$ (1.4 : 1) $C_{30}H_{62}$
$C_3H_7CO_2H$ $C_{15}H_{31}CO_2H$	1.5 : 1	$C_{18}H_{38}$ (1.4 : 1) $C_{30}H_{62}$
$ClCH_2CO_2H$ $C_{15}H_{31}CO_2H$	1 : 1	$C_{16}H_{33}Cl$ (1.1 : 1) $C_{30}H_{62}$

It is very remarkable that monochloracetate ion, which has hitherto[1] been considered never to give off $-CH_2Cl$ radical even for a moment, but immediately to decompose into $CH_2O+CO+Cl$ at the instant of its discharge, behaves in a manner exactly analogous to acetate and other fatty acid ions, when electrolysed in the presence of higher fatty acids. There remains, therefore, no room to doubt the primary formation of the chloracetyl radical in the electrolysis of chloracetic acid. The reason why ethylene chloride is not formed electrolytically can be explained by assuming that the radical is more liable to undergo oxdation than polymerisation, and therefore changes into formaldehyde and chlorine without giving rise to ethylene chloride.

$$-CH_2Cl+O=CH_2O+Cl$$

The apparently different anodic reactions of various fatty acids may perhaps be attributed to the different stability and other chemical properties of the products formed by the primary anodic reaction, which must be regarded as being always the same throughout all fatty acids. What kind of substance that primary product is cannot be decided at present. Still, the authors are much inclined to believe it

1. F. Kaufler and C. Herzog, Ber. **42**, 3858 (1909); **43**, 266 (1910); C. J. Brockman, Electro-organic Chemistry, 1 Ed., p. 46.

to be the peroxide. Recently R. Matsuda[1], studying the relation between Kolbe's reaction and hydrogen ion concentration, observed the very interesting fact that Kolbe's reaction is always accompanied by the formation of a substance having a peroxide nature, and that these two actions never take place independently of each other. Evidence recently obtained by Shukla and Walker[2], showing the presence of long overlooked methane amongst the anode gases, provides another strong argument for the peroxide theory.

Experimental

1. Acetic acid and Palmitic acid

To prepare the electrolytic solution, 15 grams of palmitic acid and 5 grams of potassium carbonate were warmed with 50 c.c. of water, and to the solution thus formed 17 grams of potassium acetate dissolved in 25 c.c. of water and 5 grams of palmitic acid dissolved in 50 c.c. of 95% alcohol were added. After the bath had been cooled internally and externally the electrolytic solution was electrolysed by passing a current of 12—13 amperes to electrodes consisting of platinum plates 15 sq. cms. in area. The temperature was always maintained at 70°—75°. In the course of the electrolysis the solution was charged twice with 5 grams of palmitic acid at intervals of 4 hours, and also with some sodium carbonate to regulate the current strength. Thus the total quantity of palmitic acid taken for electrolysis was 30 grams, and that of acetic acid 10.5 grams. After the electrolysis began, the solution became gradually coloured and finally separated into three layers. The middle (alcoholic) and the undermost (aqueous) layers contained no particular substance deemed to be the synthetic product; so, only the uppermost layer consisting chiefly of hydrocarbons was taken for examination.

The uppermost layer, which solidified on cooling, was warmed in a water-bath, after sufficient potassium carbonate solution had been added in order to remove free palmitic acid and ester. This treatment was repeated several times, and the residue was well washed with hot water and dried. The dry hydrocarbon mixture was then treated repeatedly with ether, in which a lower hydrocarbon, $C_{16}H_{34}$, dissolved,

1. Bull. Chem. Soc., Japan, **7**, 18 (1932).
2. Trans. Faraday Soc. **27**, 35 (1931).

together with a small quantity of a higher homologue, $C_{30}H_{62}$. The main part of the latter remained undissolved. The part soluble in ether was fractionated twice by distilling it under 5 mm. pressure, and nearly pure hexadecane having the following physical constants was obtained:

M. P., 17°; B. P. $138°-140°_{(5\ mm.)}$, $280°-285°_{(760\ mm.)}$

The results of analysis and molecular weight determination were as follows:

0.1347 gm. of the substance gave 0.4163 gm. CO_2 + 0.1842 gm. H_2O

	Found	Calc. for $C_{16}H_{34}$
C (%)	84.29	84.96
H (%)	15.19	15.04

0.2230 gm. of the substance in 20.3056 gms. of benzene lowered the freezing point of the solvent by 0.232°.

Mol. Wt., 230 (calc., 226)

Triacontane $C_{30}H_{62}$ was identified without much trouble, as it was easily isolated in a far purer state than hexadecane, though its melting point was found to be a little lower than that given by Petersen[1].

2. Acetic acid and Stearic acid

A mixture of acetic acid and stearic acid was electrolysed under conditions similar to those given in 1, and the solution after electrolysis was also treated just in the same manner as in 1. Octadecane which was isolated, melted at 27° and boiled at 155°–160° under 5 mm. pressure and at 308° under ordinary pressure. The results of analysis and molecular weight determination were as follows:

1. 0.1241 gm. of the substance gave 0.3846 gm. CO_2 + 0.1679 gm. H_2O
2. 0.1169 gm. „ „ „ 0.3619 gm. „ + 0.1585 gm. „

	Found		Calc. for $C_{18}H_{38}$
	1	2	
C (%)	84.54	84.43	85.04
H (%)	15.03	15.06	14.96

Benzene, 24.8436 gms.; the hydrocarbon, 0.2378 gm.; Depression of F. P., 0.184°. Mol. Wt., 255 (Calc., 254)

Another hydrocarbon produced was identified as tetratriacontane, $C_{34}H_{70}$.

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1. Zeit. Elektrochem., **12**, 143 (1906).

3. Propionic acid and Palmitic acid

Of two hydrocarbons obtained by electrolysing a mixture of propionic acid and palmitic acid in an analogous way, heptadecane, $C_{17}H_{36}$, was identified as follows:

M. P., 22°; B. P., $148°-150°_{(5\ mm.)}$, $290°_{(760\ mm.)}$

Mol. WT., 238 (Calc., 240)

Benzene, 25.7705 gms.; the substance, 0.1624 gm.; Depression of F. P., 0.130°.

The results of analysis were:

1. 0.1148 gm. of the substance gave 0.3545 gm. CO_2 + 0.1570 gm. H_2O.
2. 0.1182 gm. „ „ 0.3658 gm. „ + 0.1607 gm. „

	Found		Calc. for $C_{17}H_{36}$
	1	2	
C (%)	84.22	84.40	84.94
H (%)	15.19	15.11	15.06

Another hydrocarbon was identified as triacontane.

4. Monochloracetic acid and Palmitic acid

On electrolysing a mixture of monochloracetic acid and palmitic acid under conditions similar to those employed in 1, cetyl chloride $C_{16}H_{33}Cl$ was obtained as an oil boiling at 150° under 5 mm. pressure. It decomposed when boiled under ordinary pressure. Its specific gravity at 12° was found to be 0.842. The molecular weight determined by the cryoscopic method was as follows:

0.1270 gm. of the substance dissolved in 23.0007 gms. of benzene lowered the freezing point of the solvent by 0.113°. Mol. Wt., 250 (Calc. 261).

The chlorine content was determined by reducing the chloride with sodium amalgam and titrating the sodium chloride thus formed with a silver nitrate solution.

0.2362 gm. of the substance gave 0.03078 gm. Cl.

	Found	Calc. for $C_{16}H_{33}Cl$
Cl (%)	13.03	13.63

It is perhaps superfluous to say that triacontane was also obtained besides cetyl chloride.

5. Monophenylacetic acid and Palmitic acid

Thirty grams of palmitic acid mixed with an equivalent quantity of monophenylacetic acid was electrolysed under conditions similar to those used in 1. Soon after the electrolysis was commenced, the odour of benzaldehyde became recognizable. The main product was benzaldehyde; triacontane was also produced, along with a small quantity (about 3 grams) of another hydrocarbon, which was possibly cetylbenzene, $C_{22}H_{38}$. As the quantity of it was not sufficient to allow of its purification, its identification could be performed only very roughly, thus—

M. P., 27°; B. P., $163°-165°_{(5\ mm.)}$

0.2280 gm. of the substance in 23.7920 gms. benzene lowered the freezing point of the solvent by 0.18°. Mol. Wt., 270 (Calc., 302).

The presence of the phenyl radical in this hydrocarbon was confirmed qualitatively.

From a mixture of trichloracetic acid and palmitic acid no synthetic product could be obtained, as the high temperature necessary for electrolysis of palmitic acid acted destructively upon trichloracetic acid.

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On Binomial Distribution

By

Jun'ichi Tomita

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In this paper, after a brief study of binomial distributions, a new method of graduation is proposed. As a matter of course, the fit is satisfactory when the new method is applied to a theoretical distribution as in example 1. But it should be noticed that the series obtained by this method has, in some practical cases as in example 2, far greater graduating ability than Pearson's frequency curve.

I. Properties of Binomial Distribution

Let p be the a priori probability of occurrence of an event in a single trial and n the total number of trials. When p remains constant throughout the trials, the resulting binomial probability distribution is given by

$$u_i = {}_nC_i p^i q^{n-i}, \qquad i = 0, 1, 2, \ldots\ldots\ldots\ldots, n; \tag{1}$$

where $q = 1 - p.$ (2)

If we denote the abscissa of the mean of a frequency distribution by d and the rth statistical moment of it about the mean by ν_r^1, $r = 2, 3, 4$, using the summation method of Laplace[2], we have in this case

$$d = np, \tag{3}$$

$$\nu_2 = npq, \tag{4}$$

$$\nu_3 = npq(q-p), \tag{5}$$

$$\nu_4 = npq[1 + 3(n-2)pq]. \tag{6}$$

Eliminating n, p and q from (4), (5), (6) and (2), we get

$$\nu_4 = 3\nu_2^2 - \frac{1}{2}\nu_2 + \frac{3}{2}\frac{\nu_3^2}{\nu_2};$$

1. Of course, ν_r refers to a total frequency of unity.
2. A. Fisher, The Mathematical Theory of Probabilities, 2nd ed. p. 104.

hence, if we put

$$T=3\nu_2^2-\frac{1}{2}\nu_2+\frac{3}{2}\frac{\nu_3^2}{\nu_2}, \tag{7}$$

we obtain an important property of binomial distributions

$$T-\nu_4=0. \tag{8}$$

Also we have

$$\frac{\nu_3}{\nu_2}=q-p, \tag{9}$$

$$\frac{\nu_2}{pq}=n. \tag{10}$$

II. New Method of Graduation

When a given statistical frequency distribution satisfies the conditions

$$T-\nu_4\fallingdotseq 0, \tag{11}$$

$$\left|\frac{\nu_3}{\nu_2}\right|<1\ ;^{1} \tag{12}$$

we can graduate it by the following procedure, assuming that the distribution is binomial.

First, the moments are adjusted as follows:—

Let
$$\begin{aligned}&\nu_2+\xi=\lambda_2,\\ &\nu_3+\eta=\lambda_3,\\ &\nu_4+\zeta=\lambda_4;\end{aligned} \tag{13}$$

and put

$$3\lambda_2^2-\frac{1}{2}\lambda_2+\frac{3}{2}\frac{\lambda_3^2}{\lambda_2}=\lambda_4. \tag{14}$$

Neglecting the 2nd and the higher powers of ξ, η, ζ; we get by expansion

$$\left(6\nu_2-\frac{1}{2}-\frac{3}{2}\frac{\nu_3^2}{\nu_2^2}\right)\xi+3\frac{\nu_3}{\nu_2}\eta-\zeta+(T-\nu_4)=0. \tag{15}$$

Calculating the value of ξ, η, ζ, which makes $\xi^2+\eta^2+\zeta^2$ minimum under the condition (15), we have

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1. Strictly speaking $\left|\frac{\lambda_3}{\lambda_2}\right|<1$; cf. p. 197.

$$\xi=\frac{AD}{E},$$

$$\eta=\frac{BD}{E}, \tag{16}$$

$$\zeta=\frac{CD}{E};$$

where $$A=6\nu_2-\frac{1}{2}-\frac{3}{2}\frac{\nu_3^2}{\nu_2^2},$$

$$B=3\frac{\nu_3}{\nu_2},$$

$$C=-1, \tag{17}$$

$$D=-(T-\nu_4),$$

$$E=A^2+B^2+C^2.$$

We take λ_2, λ_3, λ_4, thus obtained, as the adjusted moments.

Next, put

$$\frac{\lambda_3}{\lambda_2}=q-p, \tag{18}$$

taking account of (2), find the value of p and q, and put

$$\frac{\lambda_2}{pq}=n. \tag{19}$$

Then compute $\log(Nq^n)$, where N is the observed total frequency. Take an integer n_0 such that

$$n-\frac{1}{2}<n_0\leqslant n+\frac{1}{2}, \tag{20}$$

and adding to $\log(Nq^n)$ successively $\log\left(\frac{n-r+1}{r}\frac{p}{q}\right)$, $r=1, 2,\ldots\ldots$, n_0, we get

$$\log(N_nC_rp^rq^{n-r}), \quad r=0, 1, 2,\ldots\ldots\ldots, n_0. \tag{21}$$

When, for some values of r, $\log(N_nC_rp^rq^{n-r})$ is smaller than -2, it is generally useless to calculate the value.

It is necessary that $\left|\frac{\lambda_3}{\lambda_2}\right|<1$, because p and q must both be positive. This is the reason why we have put the approximate condition (12).

Finally, superpose the theoretical range upon the observed so that both means coincide.

Using the method of interpolation in the series of ordinates $(21)^1$, find the ordinate t at the point corresponding to the mid point of a class of the observed range. Then 10^t or the nearest integral value to it is the graduated frequency of the class.

As for the interpolation, Everett's formula[2] is used, differences of higher than the 5th order being neglected, and x being put equal to the distance between the integral point of the theoretical range and the nearest (to the right of it) mid point of the class of the observed range.

Thus the graduation finishes.

III. Numerical Examples

Let us apply this new method to frequency distributions, and see whether the fit is good or not.

Example 1. The following table shows a theoretical example, the given frequency f being the terms of the binomial series $1000 \times (0.7+0.3)^{20}$. (Figures given to the nearest unit.)[3]

Given frequency f	Entry $\log(N_n C_r p^r q^{n-r})$ $r=0, 1, 2, \ldots\ldots, 15$	Interpolated value when $x=0.1076$	Graduated frequency f'	$\frac{(f-f')^2}{f'}$
1	$\bar{1}.81810$	$\bar{1}.92601$	1	0
7	0.76759	0.84799	7	0
28	1.39306	1.44710	28	0
72	1.81817	1.85431	71 [4]	0.014
130	2.09263	2.11440	130	0
179	2.24285	2.25234	179	0
192	2.28472	2.28323	192	0
164	2.22838	2.21676	165	0.006
114	2.08035	2.05915	115	0.009
65	1.84464	1.81414	65	0
31	1.52329	1.48363	30	0.033
12	1.11662	1.06773	12	0
4	0.62329	0.56493	4	0
1	0.04013	$\bar{1}.97185$	1	0
1000	$\bar{1}.36169$	$\bar{1}.28066$	1000	$\chi^2=0.062$
	$\bar{2}.57945$			

1. We take this for the entry, because, if we put $x=i-\frac{n}{2}$, $\log u_i$ is expansible in a convergent power series of x, provided $|x|<\frac{n}{2}$.

2. H. L. Rietz, Handbook of Mathematical Statistics, p. 40.

3. G. U. Yule, An Introduction to the Theory of Statistics, 6th ed. p. 294.

4. The actual value is 71.50; we take 71 as the nearest integral value, so that the total frequency shall amount to 1000.

The constants are as follows:

mean = 5.9940	$\xi = -0.01788$	$\frac{\lambda_3}{\lambda_2} = 0.37083$
$\nu_2 = 4.19996$	$\eta = -0.00081$	$q = 0.68542$
$\nu_3 = 1.55160$	$\zeta = 0.00073$	$p = 0.31458$
$\nu_4 = 51.24033$	$\lambda_2 = 4.18208$	$n = 19.3960$
$T = 51.67982$	$\lambda_3 = 1.55079$	theoretical mean
$T - \nu_1 = 0.43949$	$\lambda_4 = 51.24106$	$np = 6.1016$

To find the value of x in Everett's formula, let

M be the point where the means coincide,

P_i be the point on the graduated (or theoretical) range whose abscissa is i, referred to the point where the frequency Nq^n stands as origin and

Q_t be the point on the given (or observed) range whose abscissa is t, referred to the mid point of the first class as origin;

then we have

$$\overrightarrow{P_6M}^1 = 6.1016 - 6 = 0.1016$$

and $$\overrightarrow{MQ_6} = 6 - 5.9940 = 0.0060,$$

$$\therefore \quad \overrightarrow{P_6Q_6} = 0.1016 + 0.0060 = 0.1076,$$

as Q_6 is the nearest mid point to P_6 (on the right of it)

$$x = 0.1076.$$

Completing the graduation and finding the value[2]

$$\chi^2 = \sum_{i=0}^{n} \left\{ \frac{(f_i - f_i')^2}{f_i'} \right\}$$

to be 0.062; we see that the fit is, in this case, satisfactorily good.

Example 2. For the following actual data and its graduation by Pearson's normal curve of error, readers are referred to the Treatise of W. P. Elderton, Frequency Curves and Correlation, 2nd ed. p. 79.

1. $\overrightarrow{P_6M}$ means the distance between the two points P_6 and M.
2. H. I. Rietz, loc. cit. p. 78.

Observation		Calculation	
Central Age for groups of 5 years of birth	Sum Assured and Bonuses ÷ 1000 f	Entry $\log (N_r C_r p^r q^{n-r})$ $r=0, 1, 2, \ldots\ldots, 13$	Interpolated value when $x=0.7998$
17	11	0.22054	0.98769
22	48	1.15960	1.66290
27	124	1.76341	2.08991
32	213	2.15398	2.34581
37	281	2.37899	2.45620
42	295	2.46226	2.43554
47	185	2.41636	2.29070
52	104	2.24701	2.02322
57	40	1.95471	1.62952
62	15	1.53484	1.10009
67	3	0.97641	0.41633
	1319	0.25842	$\bar{1}$.54408
		$\bar{1}$.33977	
		$\bar{2}$.12274	

Straightforward calculation gives:

mean = 4.4405	$\xi = 0.00944$	$-\frac{\lambda_3}{\lambda_2} = 0.20590$
$\nu_2 = 3.15023$	$\eta = 0.00032$	$q = 0.60295$
$\nu_3 = 0.65026$	$\zeta = -0.00051$	$p = 0.39705$
$\nu_4 = 28.57146$	$\lambda_2 = 3.15967$	$n = 13.1977$
$T = 28.39772$	$\lambda_3 = 0.65058$	theoretical mean
$T - \nu_4 = -0.17374$	$\lambda_4 = 28.57095$	$np = 5.2403$

For the value of x, we have

$$\overrightarrow{P_5M} = 5.2403 - 5 = 0.2403$$

and $$\overrightarrow{MQ_5} = 5 - 4.4405 = 0.5595,$$

$\therefore$ $$\overrightarrow{P_5Q_5} = 0.2403 + 0.5595 = 0.7998,$$

as Q_5 is the nearest mid point to P_5 (on the right of it)

$$x=0.7998.$$

Thus the following table is obtained:

	Our Method Binomial Distribution		Pearson's Method Normal Curve of Error	
	Graduated frequency f'	$\frac{(f-f')^2}{f'}$	Graduated frequency f''	$\frac{(f-f'')^2}{f''}$
17	10	0.100	13	0.308
22	46	0.087	40	1.600
27	123	0.008	104	3.846
32	222	0.365	202	0.599
37	286	0.087	282	0.004
42	273	1.773	288	0.170
47	195	0.513	214	3.930
52	105	0.010	116	1.241
57	43	0.209	44	0.364
62	13	0.308	13	0.308
67	3	0.000	3	0.000
	1319	$\chi'^2=3.460$	1319	$\chi''^2=12.370$

Turning to Pearson's "Tables for Statisticians and Biometricians (p. 26)", when $n'=11$, we find

$P_T=0.966$ for $\chi'^2=3.460$

and $P_P=0.262$ for $\chi''^2=12.370$.

Thus, we conclude that the graduation by our new method is, in this case, much more satisfactory than that by Pearson's.

The author wishes here to acknowledge his debt of gratitude to Professor T. Wada for his kindness in reading the original manuscript and for valuable criticisms.

College of Niigata

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